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THE PRESENCE OF ORGANIC MATTER AND ITS EFFECT ON IRON REMOVAL IN GROUND WATER

By

L. R. ROBINSON, JR.

Supported By

DIVISION OF WATER SUPPLY AND POLLUTION CONTROL

U. S. PUBLIC HEALTH SERVICE

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DEPARTMENT OF CIVIL ENGINEERING

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THE PRESENCE OF ORGANIC MATTER AND ITS EFFECT ON IRON REMOVAL IN GROUND WATER

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LLOYD R. ROBINSON, JR.

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THE PRESENCE OF ORGANIC MATTER AND ITS EFFECT ON IRON REMOVAL IN GROUND WATER

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Department of Civil Engineering

University of Illinois, 1964

Studies were made of several ground waters in Illinois in which the presence of organic matter was demonstrated. The concentrations of this organic matter and iron in these waters were compared with reported iron removal efficiencies by the treatment plants at these towns. A town which had always reported satisfactory iron removal was found to have a raw water with a low and fluctuating iron content of less than 1.0 mg/l and total organic extracts in the amount of about 1.5 mg/l. The towns which had reported at least occasional difficulties with iron removal were found to have raw water which contained in excess of 1.0 mg/l of iron and total organic extracts in amounts averaging about 5 mg/l.

Carbon filters were used to concentrate the organic matter from the waters studied. It was found that two filters in series, with the water acidified before it was applied to the second filter, would produce at least twice the amount of extract as the unacidified filter alone. Chloroform, ethanol, ethanol plus ammonia, and ethanol plus hydrochloric acid were used serially as solvents to extract the organic matter from the activated carbon. Each solvent in turn produced considerable extract; however, the extracts obtained with ethanol plus hydrochloric acid contained considerable

ammonium chloride and were of little value in subsequent analyses.

The extracts thus obtained were analyzed for possible interference with iron removal by filtration. Some of the extracts obtained with polar solvents were found to maintain as much as one milligram of iron in a filterable condition per mg of extract. The filters used for these experiments were 0.22μ and 0.45μ membrane filters. It was found that, if sufficient additional iron was added to a solution prior to filtration and after the first appearance of iron on the filter, practically all the iron could be filtered from the solution. It thus appeared that the interference with iron filtration was caused by colloidal dispersion and not by chelate formation as had been proposed by some investigators.

The extracts were characterized by color, odor, characteristic titration curves, infra-red spectroscopy, chemical oxygen demand, and carbon analysis by wet combustion, and found to exhibit the characteristics of humic acids or acids formed during the decomposition of vegetable matter.

The extracts were applied to raw waters taken directly from the wells under investigation. Effects on the rate of oxidation from ferrous to ferric iron and the rate of change from a filterable to a nonfilterable condition were measured. No appreciable interference was noted. Tartaric acid was used as a reference in these experiments and in the filtration study.

Three items were noted in regard to possible organic interference with iron removal by rapid sand filtration. The presence of organic matter

is apparently associated with difficulties with iron removal; but the extracts failed to exhibit interference with iron removal in the field studies. However, previous studies at the University of Illinois appear to link the passage of iron through the filters with reduction of iron in the filters. These filters in which iron was reduced were all found to have a surface slime layer. It is thus hypothesized that the actual interference with iron removal is biological activity, which is supported by the organic matter in the ground water. Thus the slime layer creates reducing conditions at the surface of the filters, which reconvert the iron to the soluble state.

ACKNOWLEDGEMENTS

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The help of the laboratory staff, especially Mr. Miles Norton, laboratory mechanic, and Mr. Steve Young, undergraduate assistant, is gratefully acknowledged.

This report was submitted as a thesis in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Sanitary Engineering under the direction of Dr. R. S. Engelbrecht, Professor of Sanitary Engineering.

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I. INTRODUCTION

A. Nature of the Problem

Iron is a common constituent of ground water in many parts of the country. Two of every three well water supplies in Illinois contain in excess of 0.4 mg/l of iron. Forty percent of the public water supplies contain iron in excess of 1.0 mg/l (1). In Arkansas, Louisiana, Oklahoma, and Texas, seventy-seven percent of the water supplies are well supplies and this well water generally has a high iron content (2). Much of the literature which will be cited later will bear out the fact that problems with iron in water supplies are fairly general throughout the world.

The recommended U.S. Public Health Service limit for iron in public water supplies is 0.3 mg/l (3). Mohler (4) reports troublesome taste and turbidity problems with water containing as little as 0.25 mg/l. Hauer (2) has cited additional reasons for limiting the amount of iron in a water supply. Iron in excess of 0.1 mg/l causes discoloration of pulp and paper in the paper industry; the rayon industry prefers the iron content of water to be below 0.05 mg/l; iron causes spots and discolorations in the tanning of leather; it discolors, clouds, and affects the taste of liquor; stains plumbing fixtures and laundered clothes; makes tea black; darkens boiled vegetables; and iron provides an energy source for iron bacteria in water mains.

Salbach (5) in 1868 first used aeration and filtration for iron removal and the first plant was constructed in Charlottenburg, Germany in 1874. An

iron-removal plant was serving Champaign and Urbana, Illinois in 1916 (6) and by 1957 there were about 170 municipal plants in Illinois providing iron removal (1). This rapid growth in the number of iron removal plants has not been limited to Illinois alone, but in other areas of high iron content as well. As the number of plants increased, so did the problems associated with the successful treatment of certain waters. In order to solve these problems, modifications of the conventional treatment of aeration, sedimentation, and filtration were tried, as were entirely different methods of treatment. Applebaum and Bretschger (7), Babcock (8), Fosnot (9), Longley (10), and others have discussed the more common methods of iron removal which include:

1. Aeration followed by filtration.
2. Aeration, sedimentation, and filtration.
3. Aeration, addition of lime to raise the pH, sedimentation, and filtration.
4. Same as three but with the addition of special coagulants in addition to lime.
5. Aeration and filtration through a manganese zeolite.
6. Filtration through a sodium zeolite without prior aeration.
7. Substitution of chemical oxidants for aeration in any of the above processes.

Van der Wal (11) has reported that iron and manganese are difficult to remove from water by sand filtration without prior floc formation. There are several references in the literature pointing to the necessity of

aeration not only to provide oxygen for oxidation of iron but to strip out dissolved carbon dioxide followed by the addition of lime to raise the pH to the alkaline range where ferric iron is the least soluble (12, 13, 14). With the iron formed as an insoluble precipitate, alum or one of the ferric salts may be added to aid in floc formation resulting in more efficient sedimentation and longer filter runs. Babcock (15) reported that sedimentation could be further improved by using an upflow clarifier to aid clarification by contact with a previously formed sludge blanket. Careful pH control in the range of 8.5 to 9.1 was essential to the successful formation of a good floc with this type of treatment on the water studied.

Several methods of oxidation have been employed for waters which appeared resistant to simple aeration. Mathews (16) has demonstrated successful oxidation and iron removal with the maintenance of a free chlorine residual in the filter effluent. Contact aerators using various media with and without injected aeration have proved satisfactory (17, 18, 19). As little as 0.5 mg/l of copper added to the water prior to filtration acts as an oxidation catalyst and aids in adsorption of iron on sand filters (11). Potassium permanganate has been found by some to be a satisfactory oxidizing agent (20, 21, 22). If a cation exchange resin is treated with manganese, the sodium is replaced with manganese to form a resin which has proved satisfactory for iron and manganese removal. The manganese in the resin is oxidized to a valence of +4 (manganic form) with potassium permanganate; and then, when iron and manganous manganese are passed through this generated resin, they are oxidized to higher insoluble forms and then removed

by filtration. When the capacity of the medium is exhausted, the filter is backwashed and then treated again with potassium permanganate. It has been found, however, that if the potassium permanganate is added to the water to be treated prior to filtration, the filter can be operated continuously until increased head loss dictates the necessity of backwashing.

Ion exchange or the use of the zeolite process for iron removal as well as for softening has been practiced in some instances but the zero hardness water and the increased cost of softening 100 percent of the water is somewhat of a drawback. Davy (23) reported that several towns in Wisconsin have had no trouble with complete hardness reduction; however, the pH must be controlled between 8.2 and 8.4 to control corrosion. This writer has observed that the same procedure is used satisfactorily at Atwood, Illinois. Will (24) stated that some iron will remain on the zeolite even after regeneration and he recommended aeration and sedimentation ahead of softening to reduce this difficulty. Accumulated iron can be removed by treating the filter with 10 percent hydrochloric acid.

No matter what method of iron removal is employed, difficulties and incomplete removal often are apparent. As early as 1909, Weston (25) noted that colloids so small that they would not settle out of a water interfered with iron sedimentation. In 1914, he said that "certain kinds of organic matter . . . humic acids . . . interfere with coagulation of iron when the water is excessively aerated (5)." Since that time there have been many references to colloidal interference with the removal of iron. Chemical coagulation, with and without chemical oxidation by chlorination or

treatment with potassium permanganate, has been found to aid in overcoming this interference (16, 22, 26, 27, 28, 29, 30, 31, 32, 33). However Adams (34), Beaujean (35), Beneden (36), Boorsma (37), McCrea (38), Nordell (39), and Scharp (40) have reported the interference to be due to the formation of complexes with organic matter or chelation of humic acids with the iron and have found that conventional treatment methods will not provide adequate treatment.

In a study by Longley (10), further discussed by Engelbrecht, et al. (41), waters, both natural and synthetic, with varying concentrations of sulfate, nitrogen, alkalinity, hardness, chloride, and iron were subjected to iron removal treatment consisting of aeration, sedimentation, and rapid sand filtration in a pilot plant. Iron removal efficiency reached 99 percent in all cases and it was concluded that these inorganic mineral constituents or their concentrations have little or no effect on iron removal.

Ghosh (42) studied the rate of oxidation of iron in aerated ground water and found that small temperature changes, dissolved oxygen if present in excess of the stoichiometric requirement, sulfate, and chloride had no effect on the oxidation rate. He found that the equilibrium pH after aeration and the alkalinity were the controlling factors in the rate of iron oxidation. Using a trivariate regression analysis, he proposed the following equation for the half life of ferrous iron after oxidation (the time required for one half of the ferrous iron present to be oxidized to the ferric state):

$$T\ 1/2 = 521.854 - 0.3278 \times 10^{14} \times (OH^-)^2 - 182.931 \log_{10} \times (\text{Alk.}) \pm 8.10.$$

T 1/2 = half life in minutes.

(OH^-) = hydroxyl ion concentration in mol/1 (from equilibrium pH).

Alk. = total alkalinity as mg/1 of $CaCO_3$.

This equation was considered valid for equilibrium pH values between 7.48 and 7.78 and alkalinity values between 354 and 610 mg/1 as $CaCO_3$. Since two of the towns studied, Clinton and Deland, Illinois, were in the present study found to contain considerable amounts of organic matter, the presence of organic matter in ground water does not appear to influence the rate of oxidation of ferrous iron..

The work on ground waters in Illinois by Longley (10) seems to eliminate such inorganic mineral content as sulfate, nitrogen, alkalinity, hardness, chloride, and iron as major factors causing interference with iron removal, at least for the Illinois ground waters studied. Ghosh (42) found the rate of oxidation to be affected principally by alkalinity and pH but only the rate was affected and not the overall amount of oxidation. The question then presents itself: Is the interference then due to the presence of organic compounds in the water? If the problem lies in the presence of organic matter, is the problem one of complex formation or chelation so as to convert ferric iron to a soluble state, or is it a problem of colloidal formation and dispersion? Marsh (43) made a field study of possible interference with oxidation of iron by organic extracts. The extracts used in the study by Marsh were some of the extracts obtained by this author in the present study. Marsh reported that the extracts showed no interference

with oxidation of the iron in ground waters even in concentrations much higher than those found naturally.

B. Purpose and Scope of the Study

This study was designed to answer the question: Are there organic compounds present in well waters which interfere with the removal of iron by aeration, sedimentation, and filtration?

The first step in answering this question was to determine if there was actually any organic matter in the well water in Illinois. For the study, cities in Illinois were selected which had reported some difficulties with iron removal. As a control or reference, a study was also made at Philo, Illinois where satisfactory iron removal had always been reported.

Organic matter was extracted from the well water using a carbon filter and then extracted from the activated carbon with suitable solvents, dried, and weighed to determine the amount of organic matter obtained. The organic matter thus obtained was then dissolved in water to which iron was added. The water was then membrane filtered to determine how much iron could be held in a filterable condition by a given amount of organic extract. Plant operational records were also compared with the above information to determine the correlation between the presence of organic matter and effectiveness of iron removal treatment.

Field tests were then made to determine if the organic matter naturally present in the ground water or if addition of extracted organic matter could hold iron in natural waters in a filterable condition even after

aeration, sedimentation, and filtration through a membrane filter.

A correlation seemed to exist between the presence of organic matter and iron removal efficiency. This possible correlation was not apparent for the water at Atwood probably because of the practice of treating all the water by cation exchange. Therefore, the extracts were characterized by measuring their chemical oxygen demand, by studying their infra-red spectra, and their titration curves. Further characterization was made using paper chromatography and polarography. These extracts exhibited the characteristics of the hydroxyl acids commonly called humic acid. Thus, the study of these acids as they affect the removal of iron from well water is the subject of this thesis.

II. PRESENT KNOWLEDGE AND THEORETICAL CONSIDERATIONS

A. The Inorganic States of Iron in Water

Iron is abundant in nature, composing about five percent of the earth's crust. It exists mainly as anhydrous ferric oxide or hematite, Fe_2O_3; but also in a number of hydrated forms and in combination with other anions. Other forms are turgite, $Fe_2O_3 \cdot 0.5H_2O$; gothite and lepidocrocite, $Fe_2O_3 \cdot H_2O$; limonite, $Fe_2O_3 \cdot 1.5H_2O$; xanthosiderite, $Fe_2O_3 \cdot 2H_2O$; limnite, $Fe_2O_3 \cdot 3H_2O$; magnetite, Fe_3O_4; siderite, $FeCO_3$; pyrite, FeS_2; and, in addition, iron is usually contained in the silicate minerals of dark-colored igneous rocks, in the cementing material in sandstones, and in shales and most carbonate rocks (10, 44, 45).

Bass Becking, et al. (46) and Schoeller (47) have reported that all natural environments fit into a limited area of pH - Eh values and that the pH, Eh, and carbon dioxide and sulfate concentrations dictate the types of iron present in nature. Hem (48) has also reported that in the absence of excessive carbonates or chemical complexing agents, pH and iron content of a ground water serve as indicators of the Eh of the water in its natural state. The Eh, or the measured electrode potential in volts with reference to the standard hydrogen electrode, is an indication of the oxidation-reduction potential of the water at the instant of measurement; however, as pointed out by Stumm in a discussion of Hem's article and in a study by Komolrit (49), ambiguous interpretations of Eh measurements in natural waters are all too possible and a selective electrode system is

needed. Low Eh values are encountered where reducing conditions exist. Reducing conditions are usually created by microorganisms even to the extent of reducing iron from the ferric to the ferrous state at the ground surface by some facultative heterotrophs. Under these conditions of low potential, iron exists in the ferrous state and, as the Eh is raised by the addition of oxygen or some other oxidizing agent, ferric iron becomes more and more predominant. Ferrous iron is generally more soluble than ferric iron with the solubility being greatly affected by pH. Hem and Cropper (50) have developed a stability-field diagram of the state of iron in water as a function of Eh and pH. The amount of iron that theoretically could be present in solution is generally below 0.01 mg/l if the pH is between five and eight and the Eh is between 0.30 and 0.50 volts. However, at a pH of five and an Eh of 0.30 volts, ferrous iron in solution could reach a concentration in excess of 100 mg/l. From this it can be seen that, unless iron is held in solution by chelation or in suspension by colloidal dispersion, the normal pH range and dissolved oxygen content of the water treated in conventional iron removal plants should be sufficient to reduce the iron content of a water to a satisfactory level.

The reactions involved in the removal of iron from well water are not simply oxidation of ferrous ions to ferric ions followed by the formation of insoluble ferric hydroxide at neutral or basic pH values. Stumm and Lee (51) and Stumm and Morgan (52) have presented a thorough study of the various ionic states in which iron is found in water. Soluble ferrous iron occurs mainly as $[Fe(H_2O)_6]^{++}$, $[Fe(H_2O)_5(OH)]^{+}$, and $[Fe(H_2O)_3(OH)_3]^{-}$.

The solubility of these constituents is primarily controlled by the solubility of ferrous hydroxide, ferrous carbonate, and ferrous sulfide. The solubility of ferric iron is controlled in natural waters by the solubility of ferric hydroxide. The reactions of ferric iron in water are of importance not only in iron removal processes but also in processes where ferric iron is used as a chemical coagulant.

Iron usually has a coordination number of six (53) which means that it can share electron pairs with six donor atoms through coordinate bonds. The donor atoms are quite often oxygen from water molecules. Stumm and Lee (51) and Stumm and Morgan (52) reported that the hydrated ferric iron thus formed is an acid in the Bronsted sense and the complex ion reacts again with water to form the acid-base equilibrium:

$$[Fe(H_20)_6]^{+++} + H_20 = [Fe(H_20)_5(0H)]^{++} + H_30^+.$$

The conjugate base of this reaction can again transfer a proton:

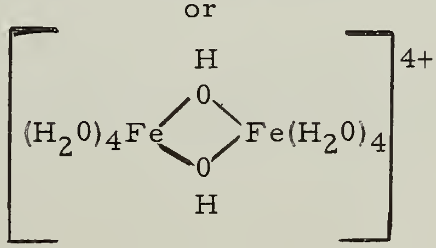
$$[Fe(H_20)_5(0H)]^{++} + H_20 = [Fe(H_20)_4(0H)_2]^{+} + H_30^+.$$

These reactions tend to decrease the pH of the solution, but in very alkaline solutions these hydrolytic reactions can continue through two more steps until the anion $[Fe(H_20)_2(0H)_4]^-$ is formed.

These ferric hydroxo complexes have a pronounced tendency to polymerize. Two molecules of the trivalent ferric ion can combine, probably through two hydroxo bridges, to form a dimeric ion.

$$2[Fe(H_20)_5(0H)]^{++} = [Fe_2(H_20)_8(0H)_2]^{4+} + 2H_20.$$

or



It has been estimated that in a 10^{-3}M solution of ferric iron only about twenty percent of the ferric iron is present in the form of tripositive ferric ion. The balance is made up of about 40 percent $[Fe(H_2O)_5(OH)]^{++}$, five percent $[Fe(H_2O)_4(OH)_2]^{+}$, and 35 percent $[Fe_2(H_2O)_8(OH)_2]^{4+}$. As a solution is allowed to stand, more and more hydrolytic (olation) reactions take place and the net charge on the iron becomes less positive. At higher pH values, the hydrolysis reactions become more involved. Riddick (54) reported that the anionic species $[Fe(H_2O)_2(OH)_4]^{-}$ becomes predominant to the point where the iron in suspension exhibits a net negative charge. Polymerization (oxolation) reactions or dehydration continue to take place as a solution ages leading to a progressive coordination of ferric ions through hydroxyl links until, eventually, colloidal hydroxo polymers and, ultimately, insoluble hydrous ferric oxide precipitates are formed (51, 52).

Black, in a discussion of the article by Stumm and Morgan (52), pointed out that ligands other than $(OH)^{-}$ may be present in the solvate shell of the free metal cation. Stumm and Lee (51) listed chlorine, sulfate, and phosphate as ligands which could replace hydroxide in the iron hydroxo complexes. The solubility of ferric iron at pH 7 is about 18 micrograms per liter but when the hydroxide in the complex ions is replaced by other ligands the solubility is increased. Many organic bases form strong soluble complexes with iron. In natural waters, high concentrations of organic material such as humic acids and lignin derivatives are frequently associated with high concentrations of soluble iron.

Complex formation may be at least partially responsible for the high solubility; however, it is also possible that colloidal ferric hydroxide is stabilized and protected as a sol by organic compounds.

B. The Reactions of Iron with Colloids in Water

Colloids or colloidal particles are generally defined as particles dispersed in a solvent medium which are too small to be seen with an ordinary laboratory microscope but which are larger than individual molecules. Colloids are thus particles with diameters between one micron and one millimicron (10 angstrom units). Where ions and molecules carry one or a few electronic charges, the much larger colloidal particles may carry thousands. With these larger charges complete dissociation becomes the exception rather than the rule. In fact these interactions are one of the determining factors of their behavior. As the particles increase in size from that of simple molecules, they may grow into large spheres, cylinders, rods, plates, or threads. The shape thus attained gives colloids their properties of high viscosities in dilute solutions or the formation of iridescent layers. When atoms or molecules are involved in interactions, the whole or a significant part of the whole becomes involved, but with colloids many interactions are limited to the surface. As the proportion of atoms located in the surface is significant and their number large, the total amount of interaction and its affect on the colloid often becomes very important. This unique field of chemistry is discussed in detail in volumes by Ware (55), Weiser (56), Mysels (57),

and was the subject of a recent Rudolfs Research Conference at Rutgers University (58).

Colloids can be classed in two general catagories; lyophilic or solvent-loving colloids where the two phases show a marked combining power and both phases are continuous such as starch in water, and lyophobic or solvent-hating colloids where the solvent phase is continuous and the colloids remain dispersed by forces acting on the colloidal particles such as clay or silica in water. Iron, finely dispersed in water, is of this latter type. Lyophobic or hydrophobic (water-hating) colloidal solutions or sols are the systems generally encountered in water treatment and will be the type to be considered here more fully.

Colloids are subject to three principle driving forces. Van der Waals forces are the mutual attractions between two particles brought about by the mutual repulsion of like charges of the inherent molecular polarity. With the like charges repulsed, one set of opposites is brought closer together providing an average net attraction. This charge is usually too small to overcome the surface or electrochemical forces which may either attract or repel the particles as dictated by the surface charges on the individual particles. When the electrochemical forces are of the same charge, they are quite often strong enough to prevent agglomeration of the particles. This mutual repulsion is what insures the stability of a colloidal suspension. Although colloids are much larger than simple molecules, their mass is so small that sedimentation due to the third driving force, gravity, is negligible.

The electrochemical force or charge on the surface of a colloid may be formed by the preferential adsorption of one ion of the supporting electrolyte and/or by direct ionization of some of the surface molecules. Silver iodide provides one example of how the electrolyte can affect the charge. If silver iodide, which has a definite crystal lattice, is suspended in a solution of hydriodic acid, the iodide ions in solution would be preferentially adsorbed on the surface of the silver iodide crystals and the colloids would acquire a negative charge. If silver nitrate were the supporting electrolyte, silver ions in solution would be preferentially adsorbed and the colloids would acquire a positive charge. Attracted to these charged particles are oppositely charged ions from the solution. Some of these attracted ions are held rigidly to the particles or micelles while the rest of the attracted ions form a diffuse or second layer surrounding the inner attached layer. The adsorbed ions which constitute the inner portion of the double layer are called the stabilizing or potential-determining ions and the ions which constitute the outer diffuse portion of the double layer are called the counter ions.

The total or Nernst potential on a particle is reduced with distance from the colloid surface as more and more counter ions are encountered. The reduction in potential caused by counter ions in the fixed portion of the double layer is called the Stern potential and the potential in the diffuse layer is called the zeta potential. Figure 1 is a diagram of a colloid particle showing how the potentials are established.

In order to destabilize colloids so that they can agglomerate or

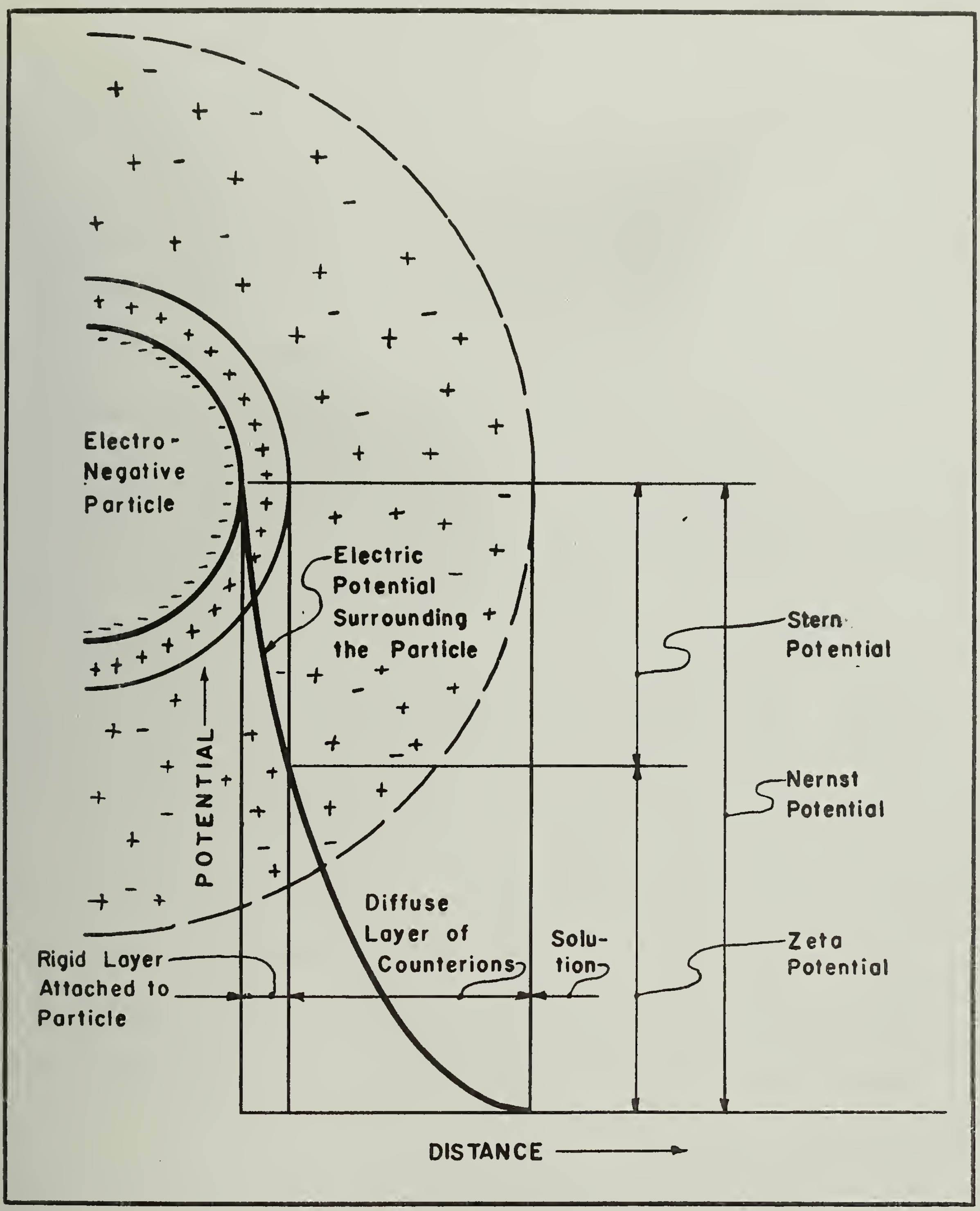


FIGURE 1

COLLOID PARTICLE

flocculate into particles large enough to be affected by gravity and settle from solution, the Nernst potential must be overcome sufficiently to allow Van der Waals forces to hold the particles when brought into contact with one another. As the Stern potential reduces the Nernst potential by the amount of the charges on the counter ions in the fixed portion of the double layer and as the fixed layer is so thin that particles so close that their fixed layers touch are usually agglomerated by mutual attraction, only the potential in the diffuse layer, the zeta potential, must be overcome in order to cause flocculation. If the zeta potential is sufficiently low, this can be accomplished by mechanical agitation and thus forcing the particles to collide. If this is not sufficient, the zeta potential must be reduced.

There are two general ways in which the charge associated with a sol can be reduced to the point where flocculation can take place. First, counter ions with a higher valence than those originally present can be added in sufficient concentration to substitute for the low valence ions originally present and thus cause a much more rapid drop in the Stern and zeta potentials. As hydrogen and hydroxl ions quite often make up a considerable portion of the stabilizing and counter ions, a change in pH can sometimes effectively lower the zeta potential. Either separately or in conjunction with the first method, the potential can be reduced by adding a similar concentration of colloids with the opposite charge and then the particles can flocculate by mutual neutralization of charges.

The valence of the counter ions is very important in determining their effectiveness in sol destabilization. It has been found that divalent

ions are about one hundred times as effective as monovalent ions and trivalent ions are about one hundred times again as effective as divalent ions. This effect of valence on the counter ions is called the Schulze-Hardy rule after the men who first enphasized it (57). Even all ions of the same sign and valence do not all exhibit the same flocculation values. The structure and especially the size of the ions dictate how easily they can fit into the colloidal structure with the smaller ions being able to fit closer and more effectively. Although all cólloids do not fit exactly into the same pattern, a general scheme of the order of effectiveness, called the Hofmeister series, has been developed. One series for the monovalent anions in decreasing order of effectiveness is: F^-, IO_3^-, $H_2PO_4^-$, BrO_3^-, Cl^-, ClO_3^-, Br^-, NO_3^-, ClO_4^-, I^-, CNS^-. One series for cations prepared for the precipitation of a silver sol is: Al^{+++}, Ba^{++}, Sr^{++}, Ca^{++}, H^+, Cs^+, Rb^+, K^+, Na^+, Li^+ (55, 57). It is to be noted that the same ion will not always be the most effective in flocculation; the total ionic makeup of the solvent system as well as the colloidal particles will dictate which ion will be the most effective under a given set of conditions.

In natural waters the charge on turbidity particles is predominantly electronegative and is often strong enough to result in sufficient mutual repulsion to cause the formation of colloidal sols. These sols consist of finely divided silt and clay, and organic matter undergoing microbial decomposition (54). Riddick (59) found these electronegative colloids to have a zeta potential in the range of 15 to 25 millivolts. Shapiro (60) in studying the yellow coloring matter of pond water, found it to be mainly hydroxy

carboxylic acids either in solution or in colloidal suspension. These are the acids which are generally called humic acids which are intermediate decay products of decomposing vegetation. One importance of these colored organic compounds is their general association with iron in water. Black, in his discussion of the article by Stumm and Morgan (52), stated that "colored waters have been collected from many parts of the country and without a single exception, the color has been found to be complexed with iron."

If the iron in a water is held in an organic colloidal complex, flocculation to destabilize the sol would be the way in which to remove the iron. Ferric iron, either as the chloride or sulfate, and aluminum sulfate or filter alum are the most common coagulants used in water treatment, so excess ferric iron should be useful in flocculating organic colloids.

Longelier, et al. (61) have studied the relationship between coagulant dosage and exchange capacity (the capacity of the counter ions to exchange with ions of a higher valence) and the affect of this relationship on floc formation. Normal floc formation occurs when sufficient counter ions and hydrolysis products are present to destabilize the sol. A more satisfactory, larger, and more rapidly settling floc is obtained when sufficient agglomerating agent of opposite charge is added. Figure 2 is a graph of the flocculation zones.

When sufficient iron is present in a solution in the ferric state, the ferric hydroxo complexes can form positive, neutral, or negative sols depending on the pH of the solution. This charge on the coagulant particles

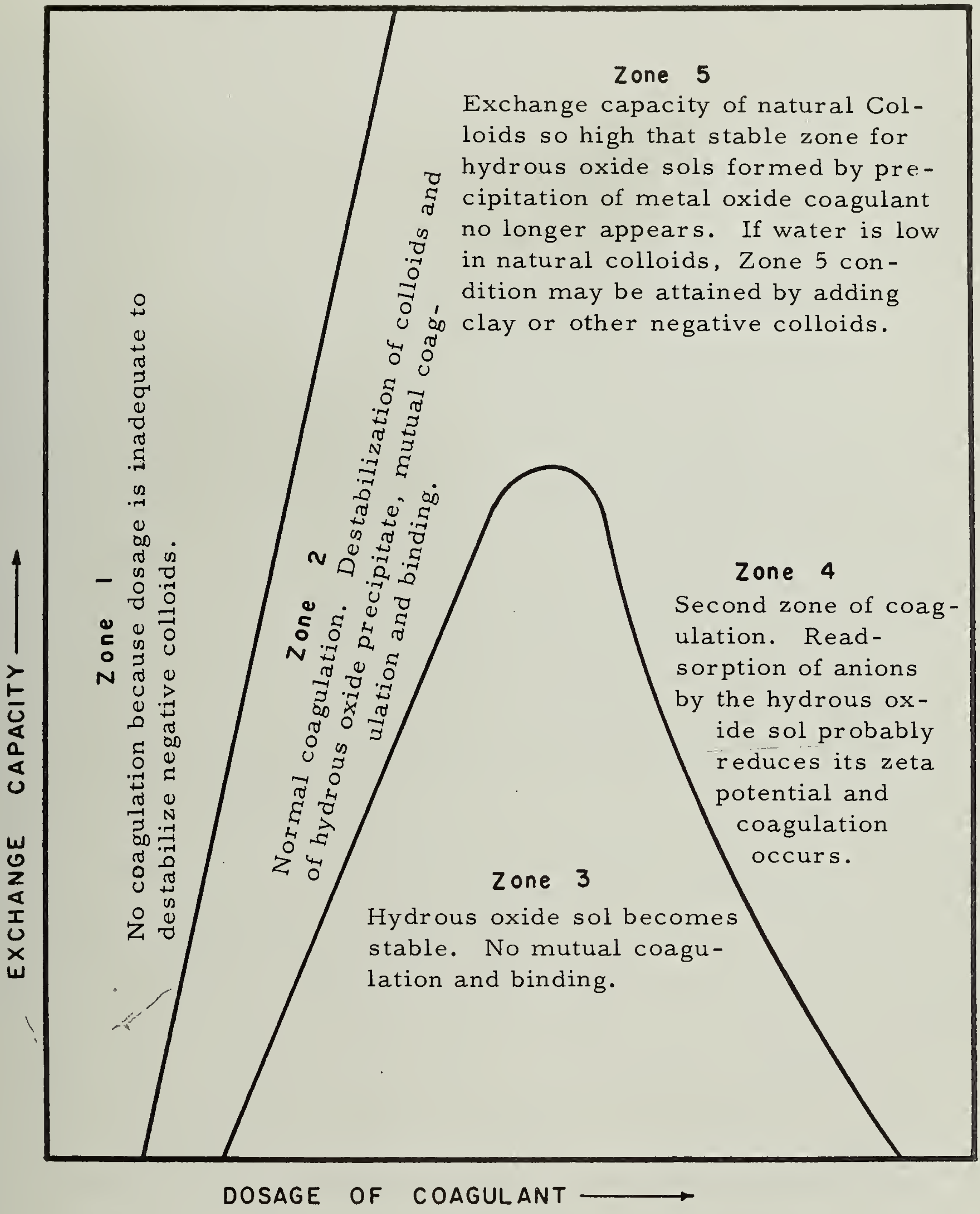


FIGURE 2

ZONES OF FLOCCULATION

becomes quite important in clarification by sedimentation. Riddick (54, 59, 62), Stanley (63), and Black, et al. (64, 65, 66) discuss methods in which electrophoretic measurements are made of zeta potentials by measuring the current of opposite direction which will just stop migration of the colloids under consideration in an electrophoresis cell. In noting the zeta potential of a solution and the efficiency of removal of unwanted colloids, the zeta potential at optimum coagulant doses and optimum pH can be determined.

Stumm and Morgan (52), Riddick (54), Stanley (63), and Riddick in a discussion of an article by Black (66) all point out that alum and ferric salts produce negative colloids in alkaline solutions. Although in natural waters the coagulants can produce floc under these conditions; their zeta potentials, which can be as high as -25 millivolts, hinder their effectiveness in removing the negative colloids present in the water. Fair and Geyer (67) summarize the practical aspects of the behavior of alum and ferric iron as coagulants as follows:

1. The pH range of relative insolubility is five to seven for alum and above four for ferric iron.
2. The presence or addition of negative ions extends the useful range of pH in the acid range. For example, sulfate ions become counter ions to neutralize any coagulant remaining after the negative colloids have been agglomerated.
3. In soft waters, negatively charged color colloids are coagulated most effectively at pH values of four or less. The trivalent ions of aluminum and iron are then the precipitating

agents. (In practice a pH as low as four is seldom attained.)

4. Stirring increases the opportunity for contact and decreases the time for floc formation. It also promotes floc growth.
5. Iron and manganese naturally present in water can be called into use as coagulants and to speed their own removal.

Riddick (54, 59, 62), and Black et al. (64, 65, 66, 68) have made studies to determine the effectiveness of polyelectrolyte coagulant aids in further reducing zeta potentials when used in conjunction with the usual coagulants. Riddick found that a zeta potential of ± 5 millivolts gives optimum turbidity removal. In order to attain this low a potential with alum or ferric salts, all the natural alkalinity would be consumed and excess coagulant would then remain in colloidal suspension. In order to prevent this, sufficient coagulant is added to lower the zeta potential to about -10 millivolts, providing that at least 6 to 8 mg/l of alkalinity still remains, and then one of the new commercial coagulant aids or cationic polyelectrolytes is added to lower the potential to zero. Using an electrophoresis cell as an operational tool should enable operators to accomplish practically complete turbidity and color removal.

As this study is related to iron removal, it is more concerned with the complete removal of the coagulant (ferric iron compounds) than with the removal of the organic colloids except as they are associated with iron. However, as can be seen from the above discussion, if the problem with iron removal is one of sol stabilization of the iron in organic colloids, then iron removal can only be accomplished by sol destabilization. Zaides (69)

studied the interaction of iron with certain organic acids. He found that the sodium salts of acetic acid and formic acid form colloidal suspensions with ferric iron while sodium oxalate forms a definite anionic complex: $Fe_2(C_2O_4)_3$. This reaction of iron with sodium oxalate points to another possible source of organic interference with iron removal. Iron has the ability to form stable soluble complexes or chelates with certain organic compounds.

C. The Reactions of Iron with Organic Chelating Agents in Water

Metal ions in aqueous solution are highly solvated with a number of water molecules having the negative (oxygen) end of their dipoles directed toward the positive metal. Some common configurations for this complex formation are tetrahedrans, square planes, and octahedrans with the metal in the center. This is an idealized condition in which the number of water molecules is only a statistical average and the number, the angles involved, and the bond distances are all a function of the metal involved, the temperature, concentration and the ionic strength. Because of the positive charge on the metal ions, one or more of the water molecules can lose a hydrogen ion with the result that a hydroxyl ion then becomes the ligand or complexing agent.

Ligands, other than hydroxyl ions, can complex with metal ions through several types of bonding. Sometimes the bonds are electrostatic such as the attraction of a positive metal ion for a negative ion or the negative part of the dipole of a neutral molecule, or the bonding can be covalent with an unshared pair of electrons from the ligand helping to fill

out the electron ring of the metal to that of an inert gas. In either case or any intermediate system, the ligand is always the electron donor while the metal is the electron acceptor. Thus it can be seen that metal ions in solution can affect pH, and pH can affect complex formation.

These complex or coordination compounds are called metal complexes if each ligand enters into one bonding with the metal ion. If, however, a ligand has two or more donor groups and forms a ring with the metal ion as a part of the ring, the resulting structure is a metal chelate compound and the donor is said to be a chelating agent. Some of the chemical and physical properties of metal chelates resemble those of the simple complexes while other properties are fundamentally different. These differences set chelates apart as a separate and distinct group of chemical compounds which have become important as aqueous sequestering agents in chemistry, biology, and agriculture. Books by Martell and Calvin (70), Chaberek and Martell (71), and one edited by Wallace (72) present a thorough description of the current knowledge concerning the chelate compounds.

Many metals can react with chelating agents but only the strongly non-metallic elements of Groups V and VI in the Periodic Table of the Elements can serve as the donor atoms. Nitrogen, sulfur, and oxygen are the only common examples. Covalent compounds with a metal bonded directly to a carbon atom are called organometallic compounds and are an entirely different class of compounds. There is a definite order of stability of the complexes as influenced by the metal involved, irrespective of the nature of the ligands considered; for the trivalent metals in order of decreasing

stability: Tl, Fe, Ba, Al, Cr, and for bivalent metal ions: Pd, Cu, Ni, Pb, Co, Zn, Cd, Fe, Mn, Mg. These are not all the metals which can form chelates. A complete list with their common coordination requirements can be found in the literature (70, 71). Iron in either the ferrous or the ferric state commonly has a coordination number of 6 which accounts for iron hydrolyzing with six molecules of water in aqueous solutions.

The properties of metal ions in aqueous solutions become altered when they become chelated. Chelation decreases the tendency toward olation or the building of high molecular weight metal hydroxyl complex ions. Olation is not entirely eliminated as a number of olation reactions have been observed with some metal chelates.

When metal ions are masked from the solvent water by the chelating ligands, the solubility becomes that of the chelating agent. If ionizable groups are present making the chelating agent water soluble, the metal chelate formed is also water soluble. The only apparent change in the solution might then be a typical color formed by the chelate. Shapiro (60) in his studies of lake water found that, although at pH 7 the solubility product for iron is 4×10^{-8}, as much as 0.03 mg/l was actually in solution. This ability to increase the solubility of iron in solution is called sequestering and the chelating agents involved are sequestering agents. Wallace (72) reports that organic chelates in increasing the solubility of iron provide a method for vegetative plants to obtain iron from the soil as iron chelates. Chelating agents such as ethylenediamine tetraacetic acid (EDTA) provide metals with solubility and definite color changes to the extent that

they can be used as indicators for the quantative determinations of such metals as calcium and magnesium. Chelating agents like orthophenanthroline produce color in proportion to the amount of metal entering into chelate formation and can thus be used for the colorimetric determination of such metals as iron.

The increase in electron density surrounding a chelate increases the tendency of a metal to oxidize to a higher valence and thus increases the oxidation potential. Also, as these complexes are usually negative, an increase in oxidation state of the metal results in a stabilizing reduction in the charge of the complex. The tendency to form stable electron configurations in the orbitals may result in either an increase or a decrease in the oxidation potential. In order to complete the available orbitals, the lower valence state for iron is favored, but the high negative charge on most natural chelating agents, aids in maintaining iron in the ferric state. The phenanthroline compounds have sufficient positive charge to reverse the potential, and thus insure that iron will remain in the ferrous state which is essential for proper color development in the quantative determination of iron.

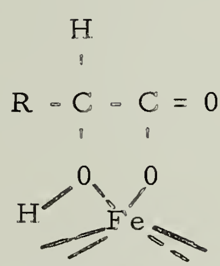
Chelation of metal ions may also affect the rate of chemical reactions through specific catalytic action of the chelate compound or by the reduction in concentration of free metal ions to give an "unreactive" chelate compound.

In the introduction it was pointed out that many instances have been reported where iron is present in natural waters complexed with organic

compounds generally classified as humic acids. Febeck (73) defines a humic acid as "soil organic matter sufficiently degraded so that its source and original structure are no longer identifiable." He was able to account for 20 percent of the organic component of a soil by using gas chromatography and found oxygen containing compounds containing carboxyl groups. He found that these organic compounds combine with minerals to create soils rather than merely mineral aggregations. These organic compounds were also found to permit biological activity, provide a source of nitrogen, phosphorous, sulfur, and trace elements, and increase the tilth, aeration, and water holding capacity of soil. Chelate compounds and their functions can explain, at least in part, all of these phenomena. Walther (74) extracted humic acids from Minnesota peat and found them to be a heterogenous mixture of nonspherical molecules which are probably hydrated polyelectrolytes. Their molecular weights range from 2×10^4 to 3×10^5 and they contain a wide and continuous range of ionization constants. Scharp (40) found that the strongest complexing agents are ions of the smaller dicarboxylic and the alpha-hydroxy carboxylic acids. He further stated that when two acidic groups are close enough to be mutually interacting, strong chelates are formed with iron. DeKock (75) demonstrated that iron complexed with EDTA or a water extract of peat promoted a translocation of otherwise insoluble iron in plants. Muller (76) observed carboxyl and hydroxyl groups to be the sights of base exchange in humus and Waksman and Iyer (77) found that one gram of ferric oxide could be complexed by from 0.9 to 2.79 grams of humus.

Shapiro (60, 78, 79) in his study of the yellow coloring matter of pond water found it to be hydroxy-carboxylic acids with an average molecular weight of 456 and an equivalent weight of 228 as compared with soil humic acids which have an average molecular weight of 1400. The lakes he studied contained between 4.5 and 9.0 mg/l of humic acids, which he concluded were not chelates because they were not dialyzable and would not pass through a 0.10μ filter. This does not necessarily eliminate the possibility that chelates are formed and then are hydrolyzed into larger particles with colloidal properties. Adams (34) found hydroxy-polybasic acids such as citric, tartaric, and malic acid to interfere with iron sedimentation.

Chaberek and Martell (71) indicate that the most important classes of sequestering agents are those which can form five- and six-membered chelate rings. Four-membered rings are rather rare. Rings containing more than six links are generally unstable. It can thus be seen that the alpha-hydroxy carboxylic acids can form stable five-membered ring chelate compounds such as:



In this type of reaction the iron replaces the proton from the carboxyl group and thus lowers the pH of the solution. Conversely, in very acid solutions, chelate formation would be greatly hindered.

The foregoing discussion points to three possible sources of

interference with iron removal by aeration, sedimentation and filtration. They are:

1. The formation of soluble hydroxo polymers of iron.
2. The formation of colloidal dispersions with organic colloids.
3. The formation of soluble chelates with organic sequestering agents.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Isolation of Organic Matter from Ground Water

Several methods have been successfully used to remove and isolate organic matter from natural waters in order to make chemical characterizations and quantitative measurements of the concentrations of organic matter present. The method in most general use is to pass the water to be analyzed through an activated carbon filter. The organic matter, which is adsorbed on the carbon, is then extracted with suitable solvents. After the solvents are driven off by evaporation, semi-quantitative measurements can be made of the organic residue and the extracts can be used for further characterization. Middleton, et al. (80, 81, 82) at the Robert A. Taft Sanitary Engineering Center have done considerable work with carbon filters. They found that a standard carbon filter (which will be described later) removed 63 percent of the organic matter from filtered city water at Cincinnati, Ohio and 82 percent of the organic matter from raw water from Nitro, West Virginia. Various solvents have been used to extract the organic matter from the carbon. Middleton, et al. (81) found that extraction with chloroform followed by extraction with ethanol obtained the greatest recovery of organic matter adsorbed from river water.

As the carbon filter technique does not recover 100 percent of the organic matter present in a water, it does not give absolute quantitative results. However, it can be used to establish a base concentration of organic matter present to use as a reference and then for monitoring

organic pollution and changes in concentration. In order to obtain higher yields of organic extract, Myrick and Ryckman (83), Sproul and Ryckman (84), Atkins and Tomlinson (85), and Spicher and Skrinde (86) have used filters containing from 1.3 to 2.0 cu. ft. of carbon instead of the 0.074 cu. ft. in the standard filter; however, they were designed for the same contact time. As adsorption efficiency is higher for waters of low turbidity and as the water used in their studies came from the Missouri River at St. Louis, Missouri, the water was presettled and filtered through a diatomite filter before it was applied to the carbon filters. Sproul and Ryckman (84) reported that the adsorption efficiency drops off above pH 8.5. Therefore, they maintained the pH between 7.0 and 7.5 for maximum adsorption. Hyndshaw, et al. (87) used activated carbon to remove odors from a water supply and found that the efficiency was only 10 percent at pH 10.6 and increased to 70 percent at pH 9.6. Spicher and Skrinde (86) found that, if the effluent from a carbon filter was acidified with sulfuric acid to pH 3.2, at least twice as much organic matter was obtained as with the first filter alone. Middleton (80) also made this same observation. The Water Research Association, at Buckinghamshire, England (88) obtained a high recovery of colored organics from some lakes by using a combination of activated carbon mixed with an anion exchange resin. The extracts were eluted from the filter with sodium chloride, but the sodium chloride was difficult to remove from the extracts.

Bikerman (89), in discussing the adsorption of organic liquids on activated carbon, has stated that the relative size of pores on one hand

and of the molecules of solvent and solute on the other influences the accessible surface area of the carbon. Carbon is activated by heating at high temperatures in an atmosphere of carbon dioxide. All types of activated carbon adsorb uncharged molecules, but, when significant amounts of ash remain, ion exchange reactions take place. With very little ash present, adsorption of charged ions is by hydrolytic or electrochemical action. Adsorption is a process at the carbon-liquid interface and usually is so rapid that the efficiency is not greatly dependent on the rate of application.

Shapiro (60, 78, 79, 90), has made extensive studies of the yellow coloring matter in several lakes in New England. His usual process of concentration is a freezing-out technique. A sample to be concentrated is continuously stirred while being frozen. As the water freezes, the central, unfrozen core becomes more and more concentrated containing about 99 percent of the impurities in the water. A twenty to one concentration has been made in this manner. The concentrate is applied to a hydrogen ion exchange resin after having been filtered through a 0.45μ membrane filter. The organics, freed of their metal cations, are eluted with n-butanol and dried under a vacuum.

Shapiro (60) and Mueller, et al. (91, 92) have used vacuum distillation to concentrate the organic matter in surface waters. Shapiro extracted the organic fraction with a mixture of ethanol and hydrochloric acid, redissolved in hydrochloric acid and then re-extracted with ethyl acetate. Mueller and his co-workers extracted the organic fraction with ethyl ether and then used silicic acid column chromatography to separate the organic

matter into distinct fractions.

In choosing a method of extracting the organic matter from well water for this study, it was desired to find one which would be relatively quantitative for the organic matter present and still be free of iron in order to permit a study of the interaction of the organic matter obtained with iron. It was decided to first try variations of the carbon filter method since it had been so widely used with apparent success. The vacuum distillation method and the freezing-out method tend to limit recovery to organic compounds which are soluble in solvents which can be used in liquid-liquid separations. Also, as the concentrates would necessarily contain a high concentration of inorganic material, the possibility of considerable inorganic carryover during solvent extraction seemed highly possible. It was hoped that, with the lower concentrations during adsorption on activated carbon, there would be a greater selectivity for organic matter which would eliminate the necessity of using a cation exchange resin to remove metal ions from the extracts.

B. Experimental Technique for Isolation of Organic Matter from Ground Water

In order to obtain more complete adsorption of the organic matter in the water, two carbon filters were connected in series with sulfuric acid injected after the first filter. The pH of the water, as it was applied to the second filter, was maintained between 2.5 and 3.0. A check on the amount of organic matter passing the acidified filter was made by adding

a third filter into the series during two of the experiments. Figure 3 is a diagram of the filter arrangement as it was used in the field. The system consisted of:

1. A flow regulator valve.
2. The raw water sampling tap.
3. Rubber hose connecting the flow regulator valve with the first filter.
4. The unacidified filter hereafter called filter A.
5. Filter A effluent sampling tap.
6. Hose connecting filter A with the water meter.
7. A 3/4 inch water meter used to meter the flow.
8. Hose connecting the water meter with the acid injection tee.
9. The acid injection tee.
    a. Five gallon plastic bottle containing approximately 0.8 N sulfuric acid.
    b. Siphon tube from acid bottle to Sigma* pump.
    c. Sigma pump connected through a low ratio pulley drive to electric motor.
    d. Rubber hose connecting Sigma pump to the acid injection tee.
10. Hose connecting tee with the first acidified filter.
11. First acidified filter hereafter called filter B.

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* The Sigma pump is manufactured by Sigmamotor, Middleport, New York.

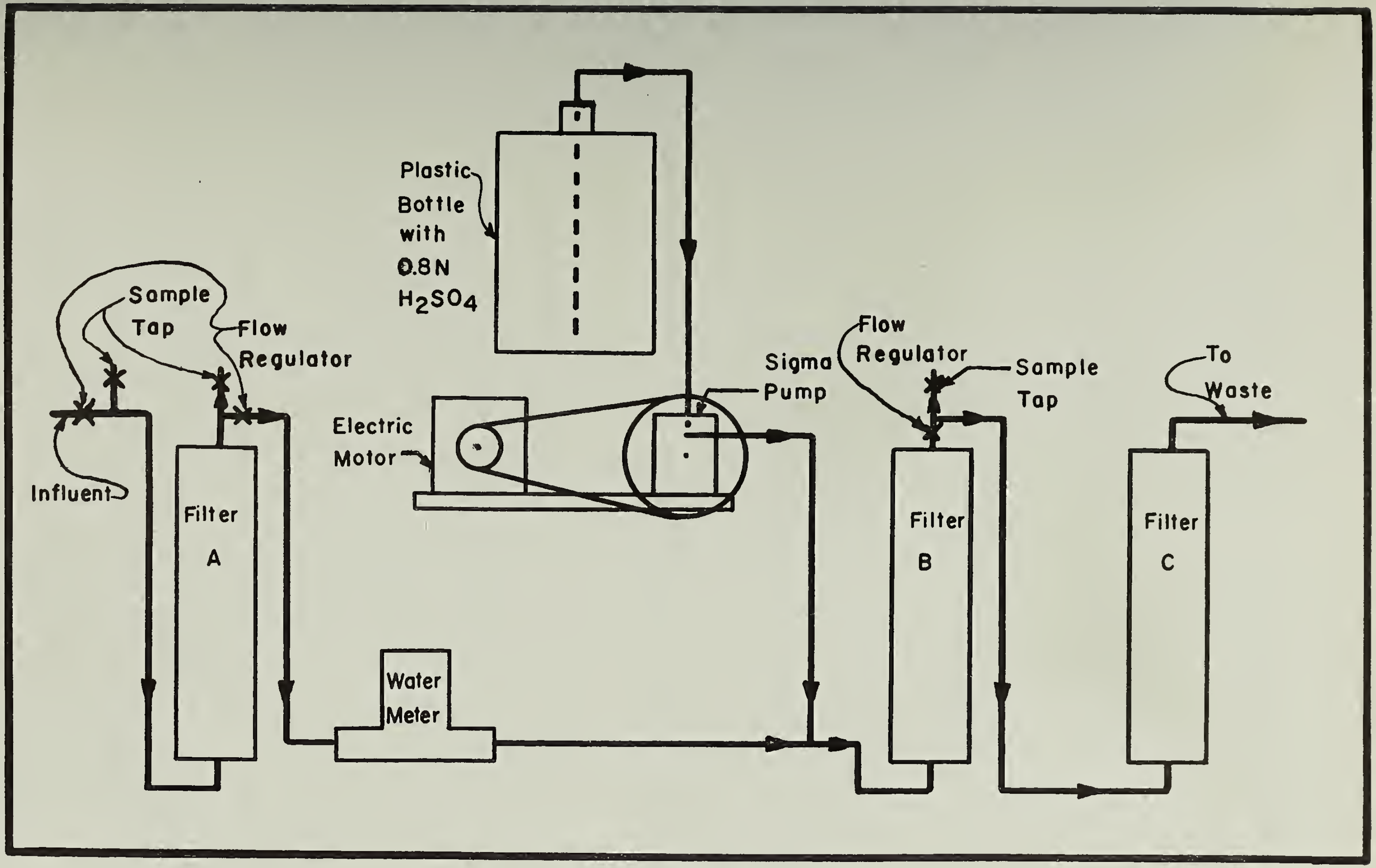
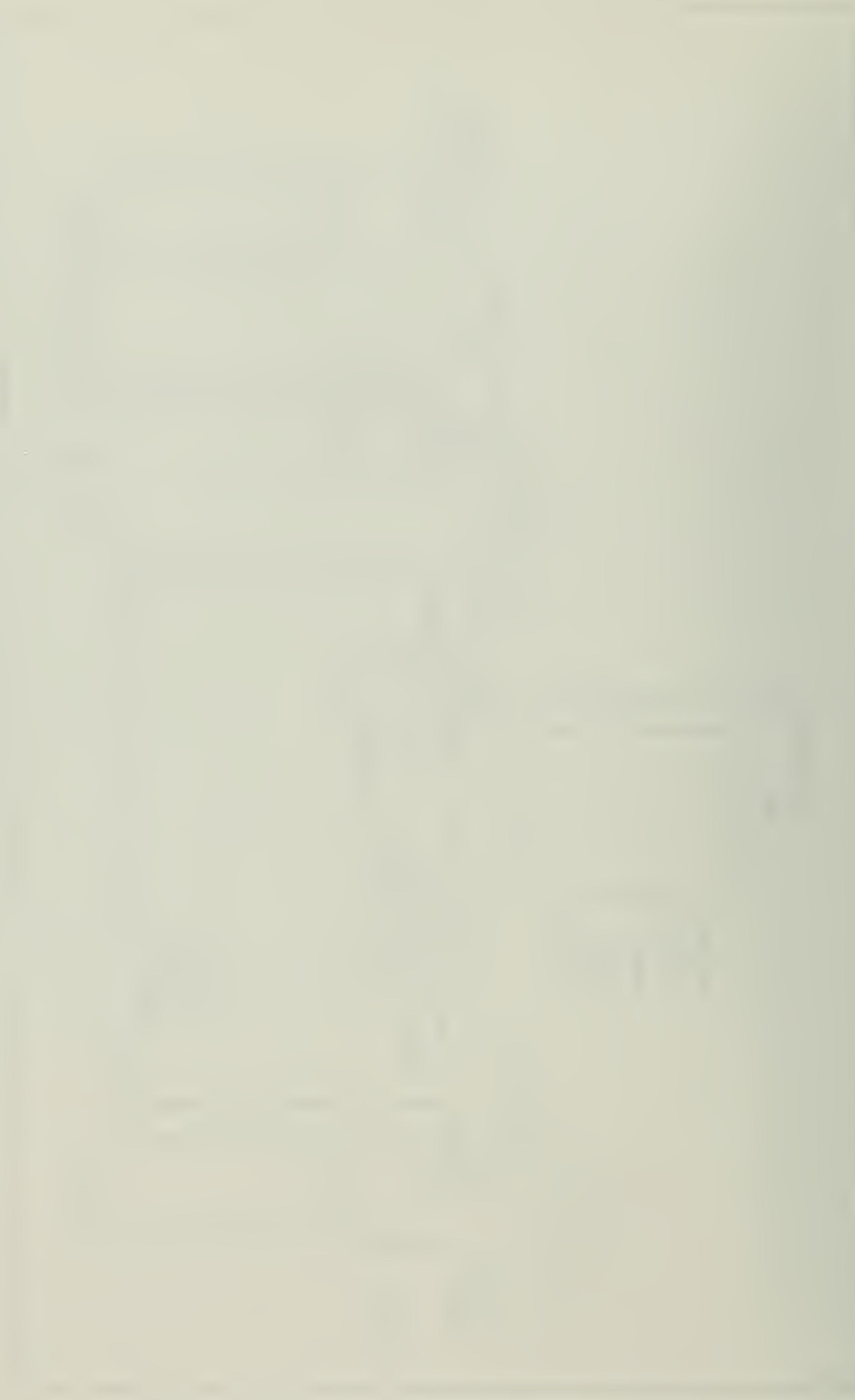


FIGURE 3

FILTER ARRANGEMENT



12. Filter B effluent sampling tap.

13. Hose connecting filter B with the second acidified filter.

14. Second acidified filter hereafter called filter C.

15. Effluent hose. When filter C was not used, the hose normally connecting filter B with filter C was used as the effluent hose.

All hoses and valves were 3/4 inch except those leading from the acid bottle to the acid injection tee.

Filter A was a standard glass filter, as described by Middleton, et al. (81), made up mainly of commercially available parts. It is detailed in Figure 4. Filters B and C were fabricated locally from lucite plastic. They are detailed in Figure 5. Figure 6 shows the sampling equipment in operation in the field.

The filters used were all charged with a 400cc layer of dry Cliffchar* of 4 to 10 mesh size, and then filled with approximately 1700cc of 30 mesh dry Nuchar C-190*. The Cliffchar served as a coarse filter for removing any turbidity which might otherwise clog the filters. The carbon was extracted with chloroform and ethanol prior to use to insure that there were no organic contaminates present in the activated carbon which could give a false indication of the presence of organic matter in the well waters tested. The extraction procedure was the same as for extraction of the filters after use. This procedure will be discussed later.

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* Both Cliffchar and Nuchar are products of West Virginia Pulp and Paper Company.

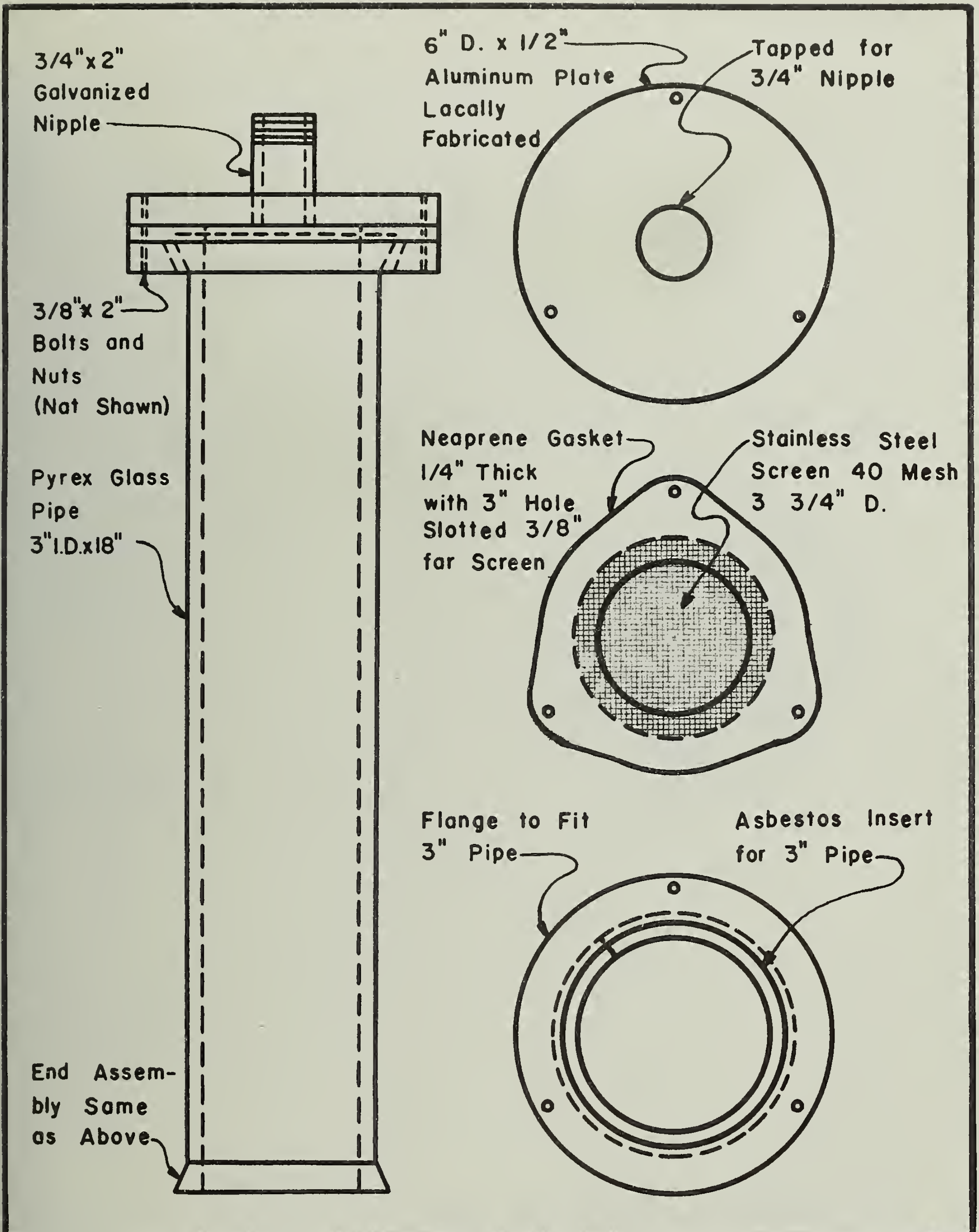

FIGURE 4

COMMERCIAL GLASS FILTER

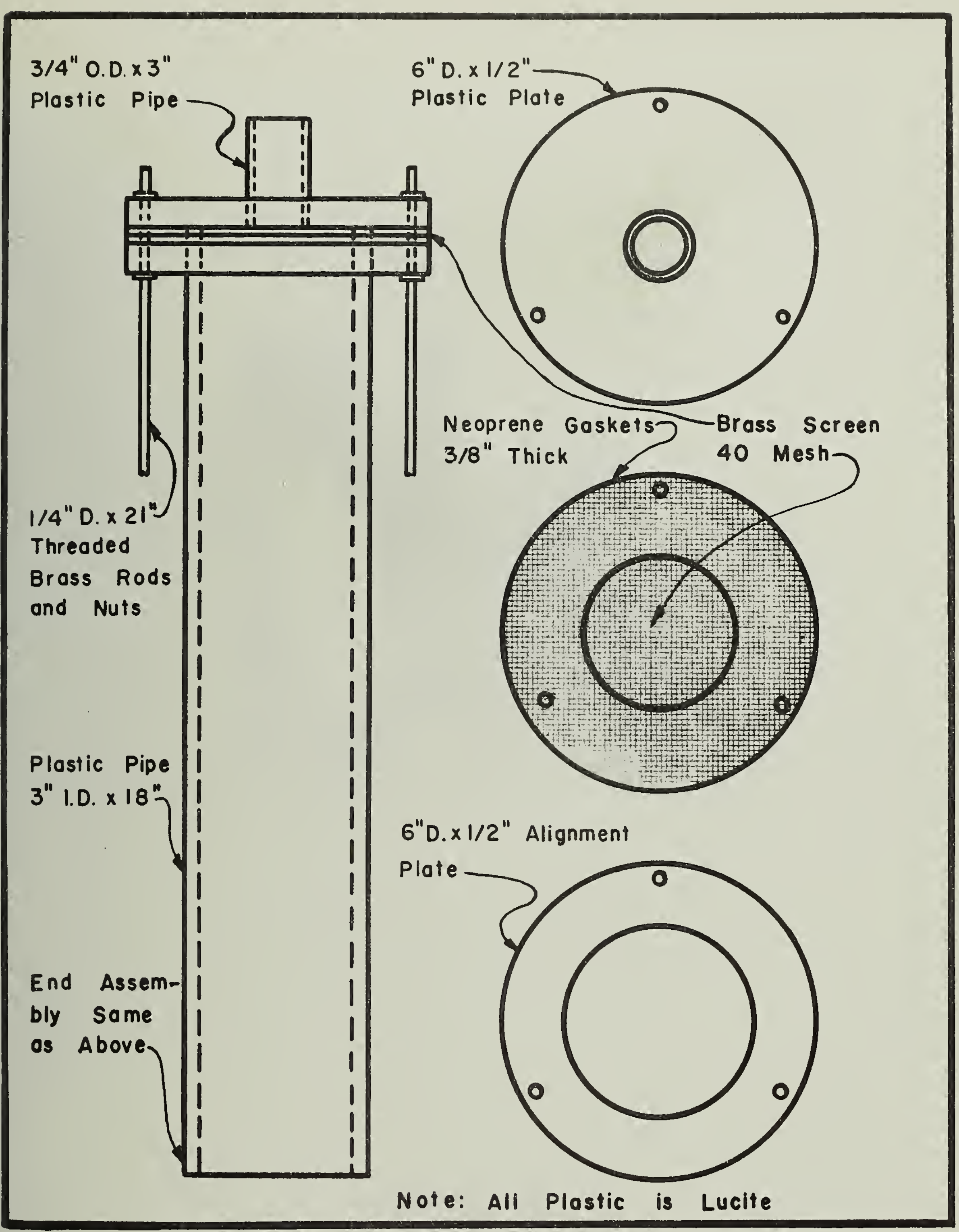

FIGURE 5

LOCALLY FABRICATED PLASTIC FILTER

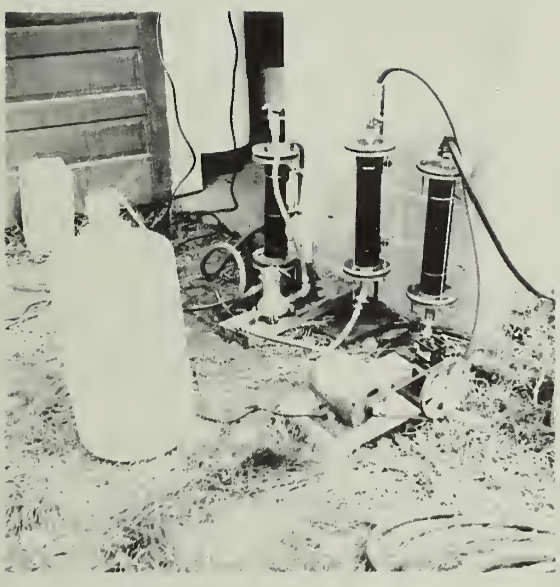

FIGURE 6

CARBON FILTERS IN OPERATION

In early experiments, a sand filter was connected directly to the raw water supply, and before the water meter. This arrangement was used so as to protect the water meter from becoming jammed by either sand coming from the aquifer with the raw water or by carbon dust from the filter. Even though the effluent from the sand filter was refiltered through a glass wool plug, fine sand passed through on every attempt to use this system. A more satisfactory arrangement proved to be the one shown in Figure 3. It was successfully used by passing about five gallons of water through filter A and discharging it through the filter A effluent sample tap before the remainder of the system was connected. The water meter never failed when this procedure was followed.

The water meter was a 3/4 inch service meter provided by the Northern Illinois Water Corporation, Urbana, Illinois. The meter was tested in the Corporation's meter shop and found to be 99 percent accurate at flows as low as 0.25 gpm.

The rate of flow was regulated by observing the time required to collect one gallon of effluent from the system. As there were no automatic flow regulators employed in the equipment and as there was no emergency shutoff provided in case of a failure of the acid injection system, frequent attention was required. For this reason, it was decided to pass the water through the filters at the rate of one gpm if at all possible instead of the 0.25 to 0.50 gpm rate recommended by Middleton, et al. (81). With this procedure, 4000 to 5000 gallons of water could be extracted in a 24 hour period. Repeated experiments were made at Clinton and Champaign

which provided some comparison of filter performance at different rates. Initial experiments were in both cases made at low rates of about 0.5 gpm and later experiments were made at higher rates of approximately 1.0 gpm. Although the quantities of extracts obtained were not identical at the two rates, they were of the same order of magnitude. As the rate chosen for applying water to the carbon filters was higher than the rate normally used, it was expected that the percentage of the organic matter in the water obtained by this method would be slightly lower than the percentage which would be obtained at a lower rate. However, from the results of the above mentioned repeated experiments and the quantities of organic extracts obtained in all the experiments, it is felt that the adsorption efficiency at the high rate is sufficiently high to provide data which could prove useful for comparison of concentrations of organic matter in various waters.

After the carbon had adsorbed organic matter from a water, it was removed from the filters, placed in trays, spread in a layer about two inches thick, and dried two or three days in a constant temperature room at 95°F. The dry carbon was then charged into large capacity Soxhlet type all glass extractors*. The bottom plates were removed and the bottoms of the extractors were packed with glass wool, which had previously been extracted with chloroform and ethanol, to prevent small particles of carbon from carrying over into the extracts. One extractor was just sufficient to handle the carbon from one filter.

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*E. H. Sargent and Company Catalog No. S-31400

Solvent was added through the carbon and allowed to siphon into the heating flasks. Two siphoning cycles were usually sufficient to add the 2500 mls of solvent needed. In addition to rapidly wetting the carbon to prevent excess heat buildup through hydrolysis, two extraction cycles were gained with this procedure. Three or four Hengar granules were added to each heating flask to insure smooth boiling. The flasks ordinarily used with the large Soxhlet extractors are three liter round bottom flasks with 29/42 ground glass neck connections. In this work, however, three liter flasks with three 24/40 necks were used. The University of Illinois glass blower removed the center necks from the flasks and replaced them with the required 29/42 necks. The side openings were used for addition of solvent when necessary, the monitoring of pH, and measurement of the boiling temperature of the solvent. The flasks were heated with three liter electric heating mantles. Power was regulated with a 115 volt variable power transformer. Because the extractors were left unattended for considerable periods of time, they were used in a laboratory hood with the exhaust fan running. Figure 7 shows two extractors in operation.

Some difficulties were observed in the use of the Soxhlet extractors. When the voltage was set too low and the boiling rate was too slow, solvent was able to drip past the top of the siphon without forcing the siphoning procedure to start. This, of course, interfered with the complete extraction cycle and reduced the extraction efficiency. When the glass wool was packed too loosely, fine carbon passed into the solvent flask; and when it was packed too tightly, the increased head loss reduced the siphoning rate to such an

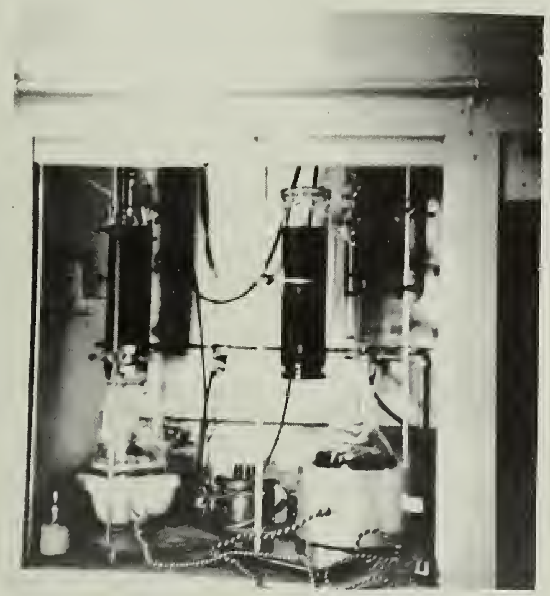

FIGURE 7

SOXHLET EXTRACTORS IN OPERATION

extent that volatilization was able to match the siphoning rate and the siphon operated continuously without allowing the extraction chamber to ever become filled with solvent. Ethanol was usually more difficult to use than chloroform, probably because of its greater viscosity. For most trouble-free operation, it was found that a setting of 90 volts provided the best rate when chloroform was the solvent being used and 100 to 115 volts was the optimum for ethanol. When carbon carried over into the solvent, it was necessary to filter the solvent before further concentration of the organic extract. It was found that vacuum filtration through Whatman No. 40 filter paper followed with several washings with the solvent being used provided satisfactory removal of the carbon.

Middleton, et al. (81) studied the extraction efficiency on Cincinnati finished water. With chloroform as a solvent and a cycle period of approximately one hour, the following results were obtained:

Number of Cycles	Percent of total amount of extract recovered
1st 5	48.3
2nd 5	26.5
3rd 7	17.6
4th 16	2.0
5th 35	3.6
6th 60	1.9

It was further reported that chloroform followed by ethanol gave about the largest recovery of extract.

In this study with the voltages noted above, the length of the extraction cycles were from 45 minutes to one hour so long as the siphon functioned properly. A solvent was cycled for about 30 hours providing about

30 to 35 cycles. This should have accomplished about 95 percent removal. When the completeness of the extractions were determined by recycling a carbon sample for 30 hours with fresh solvent, no appreciable additional extract was obtained.

For most waters, an aqueous layer formed on top of the chloroform solvent even though the carbon had apparently been completely dried. This water layer rapidly changed in color from yellow to orange to dark brown as the cycles progressed. The chloroform layer gradually changed from yellow to orange. After the extraction period had been completed, the aqueous and chloroform layers were separated with a separatory funnel and retained and studied as separate fractions. The aqueous extracts for each experiment will be called:

"Water A" (from the unacidified filter)

"Water B" (from the first acidified filter)

"Water C" (from the second acidified filter).

Correspondingly, the chloroform extracts will be called "Chloroform A," "Chloroform B," and "Chloroform C."

Upon completion of the chloroform extractions, the extractors were purged of residual chloroform by attaching an air line to the siphon tube and passing air through the carbon for about four hours. The carbon was then extracted for about 30 hours with 95 percent ethanol. In most instances the color of the solvent darkened rapidly to a very dark brown. The extracts will be designated as above with the extract from the unacidified filter being called "ethanol A," etc.

Since pH has been reported to affect adsorption on activated carbon, it was decided to try extractions with ethanol at various pH values. After the ethanol extractions were completed, fresh ethanol was added followed by concentrated ammonium hydroxide. Sufficient ammonium hydroxide was added to raise the pH to at least nine. It soon became apparent that additional extract was being obtained as the same dark brown color appeared. The extract from the unacidified filter will be called "ammonia A," etc.

After this extraction procedure was completed, the Soxhlet was purged with air for 24 hours in an attempt to remove the ammonia. The extractor was reassembled, fresh ethanol was added and then sufficient hydrochloric acid was added to lower the pH to less than two. The color change in the solvent indicated that considerable extract was being obtained, but in lesser amounts than with the other ethanol solvents. The extract from the unacidified filter will be called "HCl A," etc. As not all the ammonia had been removed from the carbon before the hydrochloric acid was added, large amounts of ammonium chloride precipitated from solution as concentration was attempted. The extracts were concentrated, filtered, diluted, reconcentrated, and refiltered but so much ammonium chloride remained that it was impossible to tell how much extract was present so the hydrochloric acid extracts were not included in the final calculations of organic concentrations in the well waters studied. A summary of the extraction scheme is shown in Figure 8.

After the solvent-extract mixtures were obtained, the solvents were driven off by distillation. The chloroform extracts were distilled at 58 to

SOLVENT	FILTER A	FILTER B	FILTER C
Chloroform	Chloroform A	Chloroform B	Chloroform C
(Water)	Water A	Water B	Water C
Ethanol	Ethanol A	Ethanol B	Ethanol C
Ethanol + Ammonia	Ammonia A	Ammonia B	Ammonia C
Ethanol + HCl	HCl A	HCl B	HCl C

FIGURE 8

SUMMARY OF EXTRACTION SCHEME

$62^{o}C$. and when the temperature started to rise, voltage on the heating mantle was reduced and the temperature was allowed to rise to $100^{o}C$. in order to distill off any residual water. As soon as the temperature started to rise above $100^{o}C$., the mixtures were transferred to tared flasks. The flasks were placed on a steam table which was swept by a stream of air from an exhaust fan. When the extracts became solidified, they were dried in a dessicator and weighed. This weight was taken as the total weight of the subject extract. With the ethanol and pH adjusted ethanol extracts, the only difference was that the original distillation temperature was $78.5^{o}C$. It was realized that any organic materials with low boiling points would be lost with this procedure. However, considering the large quantities recovered by the process used, the proportion of the extracts lost through volatilization is probably small and thus would not be expected to add greatly to the total amount of iron which could apparently be held in a filterable condition.

The process of freeze-drying with liquid nitrogen under a partial vacuum was tried, but owing to the large volumes to be handled and the apparent success with the distillation method, this method was not pursued.

The solvents used were all reagent grade, except for the 95 percent ethanol, which was technical grade received in bulk. The ethanol was redistilled before use and only that portion which came over between 78 and $80^{o}C$. was used. The solvents given off during concentration of the chloroform and ethanol extracts were collected and redistilled again for reuse. The ethanol which was collected for reuse distilled at between 78 and $80^{o}C$. and

the chloroform between 58 and 61°C. Ethanol which contained either ammonium hydroxide or hydrochloric acid was discarded as contaminated.

The carbon from one filter was divided in half and one half was extracted in the usual manner. The other half was extracted with dimethyl formamide. At the time of this test, it was not known that the ethanol plus hydrochloric acid extract was practically all ammonium chloride; therefore, the volume of extract obtained was compared with all the extracts obtained in the original procedure. Using this comparison, the dimethyl formamide extraction was not as effective as the solvent series, but, when the ethanol plus hydrochloric acid extract was excluded, it was found to be more effective. As more samples had been extracted using the solvent series before this discrepancy was noticed, the solvent series was used in all subsequent tests. The solvent series did offer the added advantage of providing some division of the extracts according to solubility.

C. Interference with Iron Removal by Organic Extracts.

As chelate formation and/or formation of colloidal dispersions were thought to be the most likely sources of interference with iron removal, it was these properties of the organic extracts which were to be determined. If the fractions causing interference had not been recovered, or if the extracts had been altered in the extraction process, measurements of the sought-after properties would be in error. However, the most probable reaction would be esterification which would have had the effect of blocking chelation sites and final results would indicate a lesser interference with iron removal.

Probably the only way in which high results could have been produced would have been through the formation of compounds which had an increased tendency to form colloidal dispersions. Therefore, any positive results obtained could probably be considered significant.

Pari and Sarup (93), Beckwith (94), and Khanna and Stevenson (95) used titration methods to measure the chelation capacity of humic acids in soils. The organic acids were titrated with a strong base with and without the addition of alkali metals. In some instances the metals displaced protons from the carboxyl groups, which caused the end point of the titration curves to be displaced. Beckwith pointed out, however, that not all acids reacted the same way. The end point was not displaced at all with some hydroxy carboxylic acids, in some instances hydroxyl groups gave up protons, and it was even possible for some metals to be present in the acids tested which blocked the reaction sites.

Khanna and Stevenson (95) measured chelation capacity by running titration curves with ever increasing amounts of the metal under consideration. The end point of the curves were displaced more and more until the chelation capacity was exceeded. At this point the curves were observed to form a horizontal shoulder, in proportion to the excess metal added, because the uncomplexed metal was consuming the hydroxide in forming metal hydroxide. This prevented the pH from rising until all the uncomplexed metal had reacted. This method of measuring chelation capacity was not always found to be satisfactory, because not all organic acids reacted the same way, and hydrolysis of some metals is too involved to

produce the simple reactions necessary for the curves to be meaningful. This procedure was attempted with two of the extracts obtained in the current study, but the addition of iron to the extracts merely produced progressively displaced titration curves with carbon dioxide free sodium hydroxide. The displacements were such that it was impossible to tell where chelation was exceeded and iron hydrolysis began.

Meites (96) and Kolthoff and Lingane (97) have prepared texts discussing the uses of the electrochemical method of polarography. Electrolysis or the occurrence of chemical reactions at electrodes immersed in solutions is characterized by the transfer of electrons between the electrode and substances in solution. This unbalance of electrons is counteracted by the migration of positive and negative ions in the solution. This flow of current is measured by the flow of electrons through the external portion of the circuit connecting the two electrodes. If the current caused by the electrode reactions is spontaneous, the system is a galvanic cell. If the reactions are forced to occur by an externally applied voltage, the system is an electrolysis cell. The cathode is the electrode at which electrons are transferred from the electrode to substances in solution causing reduction of the substance in solution. The anode is the electrode at which some of the electrolyte is oxidized. As the voltage is increased, the current flow increases. Most elements can be oxidized or reduced if sufficient voltage is applied. The minimum voltage at which an element will react is typical for given elements and compounds. The greater the concentration of the element present, the greater will be the change in the current flow.

Thus a graph of current flow at a whole range of voltages can be used to qualitatively and quantitatively identify a number of substances in a solution.

For negative potentials, a dropping mercury electrode is used with a saturated calomel reference electrode. However, at even slightly negative potentials, oxygen is reduced, producing a current flow which can mask a current flow caused by the ions under consideration. Elaborate measures must be taken to purge all oxygen from the system and keep it out during the analysis. At very positive voltages, mercury tends to dissolve from the anode; therefore, a rotating platinum microelectrode can be used for positive voltages. The platinum electrode cannot be used for negative voltages as hydrogen deposition begins at very low potentials.

As metals formed in chelate compounds have oxidation potentials different than the metal ions, polarography offers a method for measuring chelation capacity. Ferrous ion is oxidized to ferric ion at a voltage less positive than is ferrous iron complexed with organic chelate compounds. If a potential intermediate between the two values is set, no current will flow as long as ferrous iron added is chelated. As soon as excess ferrous ion is added, a current would be noted indicating the chelation capacity of the quantity of organic material originally added. This procedure using the rotating platinum electrode is called an amperometric titration. Unfortunately it does not work readily for the iron system. If the pH is high enough for the organic material to enter into chelation reactions, excess iron will, upon oxidation to the ferric state, be precipitated as ferric hydroxide instead of providing ions in solution which would produce an increase in

current. The reduction of ferric iron to ferrous iron can be measured using a dropping mercury electrode and more negative voltages. Although free ferrous iron is more soluble than ferric iron, the reaction is still quite pH dependent and changes in current flowing are too readily masked by any oxygen which might enter the reaction flask.

Finally it was decided to measure the ability of the organic extracts to hold iron in a filterable condition. This technique has been used by Shapiro (60, 78, 79, 90) in his study of the yellow organic coloring matter in pond waters. Increasing amounts of ferric iron as ferric chloride were added to a water of a controlled pH and then filtered through membrane filters. Iron was added until ferric hydroxide was observed to precipitate on the filter papers.

In the present study the extracts were dissolved in a solvent consisting of 50 percent 0.2 N potassium chloride and 50 percent dioxane. The potassium chloride was added to the extracts followed by the dioxane except, when chloroform extracts were being dissolved, the order of solvent addition was reversed. Dioxane, or diethylene dioxide, was used as a solvent aid as it is infinitely soluble in water, alcohol, ether, and most other organic liquids, and many substances which are practically insoluble in water are soluble in dioxane. This extreme range of solubility greatly assisted in putting the extracts in solution.

All solutions were prepared in the concentration of 1.0 mg organic per ml. A few of the extracts, especially the chloroform extracts, did not dissolve completely at this time. However, all of the brown color left

the particles and went into solution. All solutions were brown in color. Ten mls of each solution was diluted with distilled water to two liters, providing a working solution with an organic concentration of 5 mg/l. As will be seen later, this is in the range of concentrations of the organics in ground water. Of each of these solutions, 1500 mls was used as the test solution and the other 500 mls was retained to use as make-up solution after a portion of the original test solution had been removed to test for filterability. The solutions were stirred constantly with a magnetic stirrer and the pH was monitored continuously. The initial pH of the solutions were measured and then the pH was raised to 8.0 with dilute sodium hydroxide. At this pH, the extracts were all in solution. Pari and Sarup (93) noted that humic acids precipitate at low pH values, approximately 3.5, and alkali metal humates are formed at about pH 7.5.

In this concentration the solutions were colorless. Iron was usually added as ferrous sulfate from a stock solution which contained 1.0 mg/ml of iron held in acid solution with sulfuric acid. After the iron was added, the pH was quickly raised again to 8.0. Usually the first addition of iron was 0.4 to 0.5 mg/l and almost immediately the solutions began to turn yellow or brown. The solutions were allowed to react approximately five minutes before samples were taken; however, at no time, after the ferrous iron was added and mixed, was any ferrous iron ever found in the reaction beaker. After the reaction times were completed, 35 ml samples were filtered through 0.22μ cellulose nitrate membrane filter papers*. The

*Millipore Filter Corporation, Bedford, Massachusetts

filter papers used were 7/8 inches in diameter hand cut with a steel die to fit a stainless steel filter. An aspirator was used to provide vacuum for the filtration. The filter papers were examined for a yellowish precipitate of ferric hydroxide and the filtrates were analyzed for total iron concentration. After this step was completed, more extract solution with a concentration of 5.0 mg/l was added to the reaction beaker to bring the volume back up to 1500 mls. More iron was added and the pH was again adjusted to 8.0. Again 35 ml samples were filtered and analyzed as before. Increasing amounts of iron were added even after iron began to appear on the filter papers. The tests were stopped when iron precipitate became so heavy that filtration became difficult. As a cross check and always when iron appeared on the filter papers, total iron determinations were made on unfiltered samples.

In order to obtain larger samples for iron analysis when most of the iron was being retained on the 7/8 inch membrane filter, 75 ml samples were filtered through two inch diameter membrane filters of the same pore diameter. To test for the apparent diameter of the floc particles, 0.45μ membrane filters were used to compare filterability of the two sizes. The pH of the solutions were changed, when iron just began to precipitate, to determine the pH dependance of filterability. Samples were allowed to stand for periods up to 24 hours to see if flocculation was time dependent. Ferric nitrate was used as the iron source in some instances to see if the oxidation state, of the iron at the time it first contacted the organic matter, would cause any change. Another variable determined was the use of water

instead of the usual initial solvent of dioxane and potassium chloride.

Tartaric acid, which is a dihydroxy-dicarboxylic acid, was used as a reference of known composition. Adams (34) had reported that tartaric acid formed complexes with iron and its structure provided ideal sites for the formation of five-membered chelate rings with iron. If one end formed a chelate with iron, the other was available to ionize and insure the solubility of the chelate in water. The capacity of tartaric acid to react with iron was compared with the extracts throughout the research.

D. Field Testing of the Organic Extracts

Organic extracts, which demonstrated ability to hold iron in a filterable condition even in the ferric state, were added to well waters to determine if the same interference could be produced with natural waters. Tests were conducted at two cities where organic extracts from the water supplies had shown a definite ability to maintain iron in a filterable condition. Experiments were also conducted at a city where little organic matter was found in the well water. This water also did not present any problems with iron removal. These tests were conducted as follows:

1. A covered nine liter battery jar was completely filled with water, through a submerged tube, directly from the well under consideration.
2. The following determinations were then made:
    a. Dissolved oxygen (which was always practically nil).
    b. Ferrous iron.

c. Total iron.

d. pH (taken with electrodes inserted in rubber stoppers in the cover of the jar).

e. Temperature.

3. The jar was drained to a point where it contained eight liters after a measured quantity of organic extract was added.

4. The sample was aerated for two minutes with 2000 cubic centimeters of air per minute using a portable air compressor and a carborundum diffuser.

5. The following tests were then made at measured intervals until no ferrous iron remained in the reaction jar:

   a. Dissolved oxygen.

   b. Ferrous iron.

   c. pH.

   d. Temperature.

   e. A 35 ml sample was filtered through a 0.22μ membrane filter and total iron was measured in the filtrate.

6. An additional sample was also aerated to the same pH and the alkalinity of the water after aeration was measured on this sample. This information was used to compare the iron oxidation rate with the formula proposed by Ghosh (42).

7. In all cases, samples were taken with a siphon to protect against additional aeration during sampling procedures.

Marsh (43) used the extracts obtained in this study to further search for interferences with iron removal. In addition to the above procedures, he also ran a parallel study using iron-59 as a tracer and followed the rate of conversion of soluble to insoluble iron instead of measuring the conversion of ferrous to ferric iron.

E. Characterization of the Organic Extracts

Mueller, et al. (91, 92) separated organic acids, extracted from river water, by eluting them through a silicic acid column. Identification of some acids, separated in this manner was accomplished by using paper chromatography.

The method used for identification of dicarboxylic acids (92) was used in this study with several of the extracts and compared to several known dicarboxylic acids as a reference. The solvent system was prepared by mixing n-amyl alcohol and 5 M formic acid volume for volume. The solvent was separated with a separatory funnel into an alcoholic and an aqueous phase. The aqueous phase was retained in a beaker in the chromatography jar. After the acids were applied to the paper, the jar was sealed with the paper suspended above the solvent for one hour to allow for the atmosphere to come to equilibrium. The paper was then lowered into the solvent which was allowed to rise through the paper for about six hours. The paper was then dried for about two hours in a flowing current of air. The chromatograms were developed by spraying with a 0.04 percent solution of bromophenol blue in 95 percent ethanol adjusted

to pH 6.7. The acids appeared as yellow spots on a field of blue. The equipment used was as follows:

1. Chromatography jars, 8 3/4 in. O. D. x 18 in., with ground glass top edge.
2. Flexiglass tops drilled for stoppers through which hangers were inserted and lowered.
3. Whatman No. 40 chromatography paper cut to 14 x 16 in. with acids applied one inch up along the 14 inch side. Paper was stapled into a 16 inch long cylinder.
4. Acids were applied with melting point capillary tubes.

Takem, et al. (98) and Buch, et al. (99) have also used paper chromatography for identification of organic acids.

Gas chromatography is another technique which has been used successfully by some to identify organic material. Febeck (73) separated a number of compounds from soil extracts using gas chromatography. Lamar and Goerlitz (100) used this technique to characterize the carboxylic acids in unpolluted streams.

Even with the use of separation techniques such as those mentioned above, more elaborate methods are needed to actually identify functional groups and/or actual compounds. A satisfactory approach, currently being used, is infra-red spectroscopy. In a book by Bellamy (101) the technique is discussed and the characteristics of all the major functional groups are discussed as they appear on spectrographs. Infra-red spectrometers measure the frequencies of the vibrations of the various linkages in

molecules. As the actual frequencies of vibrations of connecting bonds can only be predicted for very simple molecules, the analyst must rely on empirical data which has been accumulated relating infra-red absorption bands with structural units in making an interpretation of a spectra. Bellamy has presented a summary of the data available and included many charts of the characteristic absorption bands for many structural units. This technique has been used by Shapiro (60, 78, 79, 90), Middleton (81), and Rice, et al. (102) in identifying some of the organic matter in water as carboxylic acids.

Infra-red spectrographs of the organic extracts from the Illinois ground waters used in this study were made in the laboratory of the Illinois State Health Department at Springfield, Illinois and in the Chemistry Department at the University of Illinois. Two methods of determining the spectra were used. The extracts were fused with potassium bromide into pellets under high pressure or they were smeared in solution on sodium chloride crystals.

In order to determine the percent organic matter in samples, various oxidation techniques have been used. Standard Methods (103) suggests that a residue from a water sample be ignited at 600°C. and the loss on ignition corresponds to organic matter plus inorganic matter lost due to decomposition and volatilization. Pickhardt, et al. (104) suggest that, for the determination of the total carbon in organic materials, the sample should be ignited at 750°C. in the presence of a copper oxide catalyst. In this study the organic composition of the extracts was made by determining

the total carbon content of the extracts. This analysis is similar to the one discussed by Prickhardt, et al. (104). This determination consisted of burning the extracts in a carbon dioxide-free environment and measuring the total amount of carbon dioxide given off. This analysis was performed by the Organic Chemistry Microanalysis Laboratory at the University of Illinois.

Chemical oxidation can also be used as a measure of the amount of organic matter in a sample. Puri and Sarup (105) used boiling potassium permanganate to measure the amount of oxidizable material in a sample extracted from soil with sodium hydroxide. They found the results to be comparable with those obtained when potassium dichromate was used as the oxidizing agent.

In this study potassium dichromate was used as directed in Standard Methods (103) except that, as the extracts were added in known weights, the results were obtained in mg oxygen demand per mg extract. Analyses of pure compounds were also made so as to determine the completeness of this oxidation procedure.

An attempt was made to classify the extracts on the basis of solubility in various solvents using the scheme described by Middleton (81). However, as this scheme is basically for chloroform extracts, and as the chloroform extracts were the least significant in the study, this method of separation and classification met with little success as almost all fractions fell in the water-soluble fraction.

Several samples were dissolved in water and used to produce

titration curves. They were titrated with 0.02 N sodium hydroxide and 0.02 N hydrochloric acid and the pH titration curves were plotted in an attempt to determine the number of ionizable groups present. Puri and Sarup (93) used this method to characterize humic acids and their results compare closely with the curves obtained in this study.

F. Chemical Analyses

In general the other chemical analyses performed in this study were carried out in accordance with Standard Methods (103). The actual methods used and any deviations made will be listed in Appendix A.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Characterization of the Waters Studied

Earlier studies of factors affecting the removal of iron from well water conducted at the University of Illinois by Longley (10), Ghosh (42), Komolrit (49), and at the Illinois State Health Department by Weart and Margrave (1), were used as a guide in selecting waters for this study. The towns of Oakwood, Clinton, and Deland, Illinois, were chosen because of reported difficulties with iron removal and persistent slime growth on filter media. This growth seemed a good indication that there was organic matter present in the water being treated. After two preliminary experiments at Deland, this location had to be abandoned because of major construction at the water plant. Iron removal at Oakwood was so unsatisfactory that the well supply was soon to be abandoned in favor of a surface supply for which a treatment plant was nearing completion at the time of this study.

Philo and Atwood, Illinois, were chosen as plants where iron removal was being satisfactorily accomplished. Philo has a low and fluctuating iron content in its raw water supply. One of the wells in operation was selected for determination of its organic content. However, when a later attempt was made to measure organic interference with iron removal, the iron content of this particular well had dropped to nearly zero. The study was then made at another well several hundred yards away. Atwood has a higher iron content in the raw water but was passing 100 percent of its water through a cation exchanger to insure a high and satisfactory degree of iron removal

as well as an unusually soft finished water. Two sets of preliminary tests were also made on the local Champaign-Urbana, Illinois, tap water, mainly for the purpose of testing the equipment before taking it into the field. This water was also known to present difficulties with iron removal from time to time. As the supply consisted of a number of wells in several different well fields, the water varied constantly in quality as the various wells were placed in and out of service. Soon after this study was completed, the iron removal treatment plant was replaced by two modern lime softening plants.

All the plants considered in this study consisted of coke tray aerators, reaction tanks, and pressure filters, except for Champaign-Urbana which had a spray aerator, reaction tank, and gravity filters. Table 1 lists the usual mineral characteristics of raw water from the wells under consideration and finished water from the treatment plants. Since, in all cases, the plants treat water from several wells, the finished water characteristics reported are for a mixture of waters. These figures have been obtained from plant operational reports on file at the Illinois State Health Department. From this table it can be seen that Philo and Atwood consistently produce satisfactory iron removal while Clinton and Oakwood exceed the maximum recommended concentration of 0.3 mg/l during a considerable proportion of the time. The mineral characteristics of the waters do not indicate any pattern which would point to an interference with iron removal. The finished water data represents data collected for the first six months of 1962.

At Clinton, Oakwood, and Philo the carbon filters were attached to raw water sample taps at the wells. The wells tested were: Clinton, Well

TABLE 1

MINERAL CHARACTERISTICS OF WATERS STUDIED
Illinois State Health Department
July, 1962

Town	Well No. and Depth	Sample Source	Total Hard. mg/l as $CaCO_3$	Sulfate mg/l as SO_4	Alk. mg/l as $CaCO_3$	Ammonia Nitrogen mg/l as N	Total Residue mg/l	pH	Total Iron mg/l
Atwood	#1 - 97'	Raw	225	0	468	1.2	513	7.3	1.8
	#2 - 96'	Raw	379		468		470		1.6
		Dist. Syst.	14 - 108					7.6 - 8.0	0.04 -0.2
Clinton	#6 - 345'	Raw	296	3.0	432	3.1	548	7.5	2.6
		Dist. Syst.	92 - 156					7.6 - 8.0	0.06-2.0
Oakwood	#3 - 72'	Raw	344		408		443		14.0
		Dist. Syst.						7.6 - 7.9	0.04-0.6
Philo	#3 - 29'	Raw	316	124	214	0	395	7.5	0.04
	#4 - 65'	Raw	297		184		373		1.9
		Dist. Syst.						7.5 - 8.0	0.01-0.2

No. 6; Oakwood, Well No. 3; and Philo, Well No. 3. As the pumps at Atwood did not run continuously, the carbon filters were attached to a faucet in the distribution system. Analyses of the waters at the time of the extractions are given in Table 2. Even though considerable iron was present in the waters at the time the extractions were made, the filters were not plugged during operation and, as will be shown later, organic extracts were obtained which contained a minimum concentration of iron.

B. Measurement and Recovery of Organic Matter in Well Water

Only one carbon filter was used to adsorb organic matter from well water in the early experiments. During these experiments, a rate of flow between 0.25 and 0.50 gpm was attempted, as recommended by Middleton, et al. (81). It was hoped that these filters would stay in operation long enough to adsorb the organic matter from about 5000 gallons of water as recommended by Middleton. In the first three experiments, the water meter was upstream from the carbon filter and was protected from sediment from the wells by a sand and glass wool pre-filter. In each instance the filter did not prevent the passage of very fine sand into the water meter. Since the meter became jammed during these experiments, the total flow through the carbon filters was estimated from the measured rates of flow and the time of operation. As the wells were out of service during these periods, estimates of total time of operation were obtained from the plant operators. These estimates were then used to translate the amounts of extracts obtained into concentrations in terms of mg/l. Using these estimates, the concentrations,

TABLE 2

ANALYSES OF WATERS AS APPLIED TO CARBON FILTERS

Town	Experiment No.	Total Hard. mg/l as $CaCO_3$	Calcium Hard. mg/l as $CaCO_3$	Magnesium Hard mg/l as $CaCO_3$	COD Start mg/l	COD End mg/l	Total Iron Start mg/l	Total Iron End mg/l	Filters
Oakwood	1	316	189	127	15.2	10.5	1.69	-	A B C
Philo	2	315	186	129	0	0	0.12	0.20	A B
	(One week later two checks on raw water iron content - 0.96 and 0.58 mg/l)								
Clinton	3	292	169	123	38.0	37.6	1.08	1.12	A B
Atwood	4	313	146	167	23.1	-	0.20	-	A B
Clinton	5	297	170	127	37.1	40.5	1.24	1.35	A B C

calculated for the two experiments at Deland and the comparison of the early estimated experiment at Clinton with the two metered experiments made later, agree fairly closely. This tends to somewhat validate the estimates. A comparison of the extracts, obtained from the early Clinton experiment with the two later experiments, and the two Champaign experiments, indicates that the carbon filters did not function as efficiently at 1.0 gpm as they did at 0.5 gpm. However, it is felt that the rather small decrease in efficiency was more than offset by the greater facility with which samples were collected. In Table 3 are listed the amounts of extracts obtained from the carbon filters during the early experiments when only one filter was in use. These preliminary experiments, in which only one filter was used, are numbered with lower-case Roman numerals to differentiate them from the more complete experiments performed later.

In Table 4 are listed the amounts of extracts obtained from the carbon filters when both unacidified and acidified water was passed through carbon filters. When filter C was used, it was found that 50 to 60 percent as much extract was obtained from filter C as from filter B. From this it is apparent that not all the organic matter applied to filter B was retained. From this, it may be assumed that the effluent from filter C may have also contained some organic matter. Thus the total amount of organic extract obtained from a water has been reported as the amount obtained from filter A plus the amount obtained from filter B and the amount obtained from filter C when it was in use. Although the total concentrations thus determined are undoubtedly less than the actual concentrations present in the

TABLE 3

ORGANIC EXTRACTS RECOVERED FROM WELL WATERS

Town	Experiment No.	Rate of Flow, gpm	Total Volume, gallons	Solvent Used	Filter A Extract gm	Filter A Extract mg/l	Total Extract mg/l
Deland	i	0.5*	3200*	Chloroform	0.9	0.07	
				Ethanol	12.0	1.0	1.07
Clinton	ii	0.5*	5050*	Chloroform	1.5	0.01	
				Ethanol	5.4	0.28	0.29
Deland	iii	0.5*	929*	Chloroform	0.5	0.13	
				Ethanol	2.0	0.57	0.70
Champaign Tap	iv	0.4	4321	Chloroform	8.2	0.50	
				Ethanol	2.0	0.12	0.72
Champaign Tap	v	0.9	5848	Chloroform	0.9	0.04	
				Ethanol	3.5	0.16	
				Ethanol + NH_3	3.6	0.16	0.36
				Ethanol + HCL	14.6	0.66	
				Dimethyl Formamide**	10.5	0.47	0.47

*Estimates
**Duplicate sample

CONCENTRATION OF ORGANIC MATTER EXTRACTED FROM WELL WATERS

Town	Experiment No.	Total Vol., Gals.	Solvent Used	Filter A Extract gm	Filter A Extract mg/l	Filter B Extract gm	Filter B Extract mg/l	Filter C Extract gm	Filter C Extract mg/l	Total Extract* mg/l
Oakwood	1	1073	Chloroform	3.6	0.89	3.5	0.87	1.7	0.41	2.17
			Water	1.3	0.31	1.8	0.45	0.9	0.23	0.99
			Ethanol	1.2	0.30	2.1	0.52	1.3	0.32	1.14
			Ethanol + NH_3	1.0	0.25	1.7	0.41	1.9	0.47	1.13
			Ethanol + HCl	6.7	1.71	4.6	1.13	17.8	4.45	
			Total							5.43
Philo	2	950	Chloroform	0.2	0.06	0.3	0.07			0.13
			Water	0.3	0.07	0.1	0.01			0.08
			Ethanol	0.6	0.17	2.8	0.77			0.94
			Ethanol + NH_3	0.5	0.13	0.8	0.22			0.35
			Ethanol + HCl	2.4	0.68	0.4	0.12			
			Total							1.50
Clinton	3	1426	Chloroform	0.2	0.04	Est.	0.30**			0.34
			Water	0.0	0.00	Est.	0.70**			0.70
			Ethanol	0.7	0.12	10.2	1.88			2.00
			Ethanol + NH_3	1.6	0.29	2.3	0.42			0.71
			Ethanol + HCl	3.5	2.49	3.3	0.60			
			Total							3.75

* Ethanol + HCl extracts not included.

** Samples lost, values used are from Clinton Experiment 5.

Town	Experiment No.	Total Vol., Gals.	Solvent Used	Filter A Extract		Filter B Extract		Filter C Extract		Total Extracts*
				gm	mg/l	gm	mg/l	gm	mg/l	mg/l
Atwood	4	1293	Chloroform	0.4	0.09	1.2	0.25			0..34
			Water	3.0	0.61	5.5	1.11			1.72
			Ethanol	2.1	0.43	4.5	0.93			1.36
			Ethanol + NH_3	1.4	0.28	4.3	0.87			1.15
			Ethanol + HCl	5.7	1.16	2.0	0.41			
			Total							4.57
Clinton	5	1153	Chloroform	0.4	0.08	1.3	0.30	0.7	0.17	0.55
			Water	0.0	0.00	3.0	0.68	2.9	0.67	1.35
			Ethanol	2.6	0.59	7.5	1.72	4.3	1.00	3.31
			Ethanol + NH_3	2.0	0.46	4.6	1.05	2.5	0.57	2.08
			Ethanol + HCl	9.1	2.09	2.8	0.64	2.8	0.64	
			Total							7.29

waters under consideration, they should be of sufficient accuracy to facilitate comparisons of the organic concentrations of these waters with waters in other regions.

The quantities of extracts obtained with ethanol plus hydrochloric acid as a solvent were not used in calculating total concentrations of organic extracts obtained from the waters because the major part of the extraction residues was found to be ammonium chloride formed by a reaction between ammonia, remaining in the carbon after the ethanol plus ammonia extrac-ions, and hydrochloric acid from the final extractions. This observation f the presence of ammonium chloride was confirmed by analyzing all eth-nol plus hydrochloric acid extracts for chloride. The extracts were found o contain from 37 to 57 percent chloride. With such a high percentage of hloride in these extracts, any adjustment in the weights obtained would ecessarily be so large that the final values for organic extracts present ould be entirely meaningless.

Table 3 reveals a large difference in the amount of chloroform xtract obtained in the two experiments at Champaign. In the first experi-ent 0.50 mg/l "Chloroform A" extract was obtained while in the second xperiment only 0.04 mg/l was obtained. This difference is probably erely a reflection of different waters being used in the experiments. The ater for Champaign is from a number of wells in several different well elds. As the same wells are not always in operation, differences in organic ncentration of the finished water can be expected to occur.

The chemical oxygen demand of the waters was measured before and

after the water was passed through the carbon filters. Table 5 indicates that organic matter was being removed from waters as they passed from one filter to the next. In comparing this data with the total amounts of extracts recovered (Table 4), however, there is no direct numerical correlation between COD and amounts of organic extracts obtained. Some samples were rendered useless because fine carbon from the filters was eluted into the sample flasks at the time of collection. This carbon gave high and erratic COD values.

As the methods used to obtain the extracts did not insure the elimi-ıation of inorganic matter, two methods were used in an attempt to deter-nine the percentage of organic matter in the extracts. The organic extracts vere oxidized chemically using boiling potassium dichromate in concentrated ulfuric acid as the oxidizing agent. Silver sulfate was used as a catalyst o insure more complete oxidation. As the samples were added by weight f volume, the chemical oxygen demand of the extracts were obtained as mg OD per mg extract instead of in mg/l. In order to see if this method would ive a true picture of the COD of organic acids, the COD values of several ıre organic acids were determined and compared with theoretical values r total oxidation. In Table 6 are given the results of this study. It is to noted that the experimental COD values for the pure compounds agree ith the theoretical values within 2.5 percent except for malonic acid which ows a difference of 10 percent. In most instances, the COD values of the tracts fell somewhere between those of the short chain dicarboxylic acids amined and pure carbon which would have the maximum COD expected of

TABLE 5

REMOVAL OF CHEMICAL OXYGEN DEMAND
BY ACTIVATED CARBON FILTERS

Town	Experiment No.	Chemical Oxygen Demand Before Filter A mg/l	After Filter A mg/l	After Filter B mg/l	After Filter C mg/l
Oakwood	1 Begin	15.2			
	1 End	10.5		9.17	
Philo	2 Begin	0.0	0.0	0.0	
	2 End	0.0	0.0	0.0	
Clinton	3 Begin	38.0	27.5	25.5	
	3 End	37.6			
Atwood	4 Begin	23.1			
	4 End			18.0	
Clinton	5 Begin	37.1	21.7	13.9	
	5 End	40.5	36.6	27.3	21.8

TABLE 6
CHEMICAL OXYGEN DEMAND OF ORGANIC EXTRACTS AND PURE COMPOUNDS

Town	Experiment No.	Extract	Chemical Oxygen Demand Measured mg/mg Ext.	Chemical Oxygen Demand Theoretical mg/mg Ext.
Oakwood	1	Ethanol A	0.71	
		Ethanol B	2.08	
Philo	2	Ethanol A	0.50	
		Ethanol B	0.12	
		Ammonia B	0.22	
Clinton	5	Ethanol A	1.27	
		Ammonia A	1.39	
		Chloroform B	1.67	
		Water B	1.04	
		Ethanol B	1.23	
Pure Compounds		D Tartaric Acid	0.517	0.533
		D Tartaric Acid	0.539	0.533
		Malonic Acid	0.680	0.615
		DL Malic Acid	0.714	0.716
		Succinic Acid	0.928	0.948
		Carbon		2.66

ample Calculations for theoretical COD:

) Tartaric Acid: $C_4H_6O_6 + \frac{5}{2}O_2 = 3\ CO_2 + 2H_2O$

Molecular weight: 150 80

$$\frac{80}{150} = 0.533 \text{ mg COD per mg tartaric acid}$$

organic compounds. From these results, it may be concluded that the extracts must be nearly 100 percent organic or it would have been practically impossible for the COD values to have been so high. These values are in the same range as those determined by Myrick and Ryckman (106) for extracts recovered from the Missouri River. Using a microchemical analytical technique, they determined empirical formulas for the chemical composition of their extracts. They determined the theoretical oxygen demand of an ethanol extract, based on its empirical formula to be 1.39 mg/l as compared to a measured COD of the same extract of 1.37 mg/l.

Total carbon analyses of several of the extracts were performed y the Organic Chemistry Microanalysis Laboratory at the University of linois. The results are given in Table 7. Using this data and the rough stimate that the extracts consisted entirely of carbon, hydrogen, oxygen, nd residue, the theoretical COD values of the extracts were calculated. he values are in close agreement with the measured values (Table 6), specially when it is remembered that the difference between the total eight of the extracts and the carbon, hydrogen, and residue was certainly not entirely oxygen. It would thus seem likely that the extracts re composed almost entirely of organic compounds or metal salts thereof, i it can be assumed that the other extracts would give similar results. he presence of ammonium chloride is again demonstrated in the ethanol us hydrochloric acid extracts by the high volatility and low carbon content in the sample analysis.

It is realized that the extracts obtained do not represent the actual

TABLE 7

TOTAL CARBON ANALYSES

Extract	Percent Carbon	Percent Hydrogen	Percent Residue	Percent Oxygen*	Calculated COD mg/mg
All extracts are from Clinton Experiment 5.					
Ethanol A	44.05	5.41	18.45	32.09	1.58
Chloroform B	57.75	6.98	5.15	30.12	1.99
Water B	37.93	4.72	9.88	48.47	1.02
Ethanol B	45.37	5.15	3.11	46.37	1.20
Ammonia B	47.71	5.52	0.87	45.90	1.27
HCl B	3.25	6.80	6.59	-	-

Sample calculations for COD:

Ethanol A: 100 percent - percent carbon - percent hydrogen -

percent residue = percent oxygen..

$100 - 44.05 - 5.41 - 18.45 = 32.09$ percent oxygen

100 mg extract = 18.45 mg residue plus

$44.05 + 5.41 + 32.09 = 81.55$ mg organic material

$$\frac{\text{Weight}}{\text{Molecular Weight}} : \quad \frac{44.05}{12} \quad \frac{5.41}{1} \quad \frac{32.09}{16}$$

Empirical formula: $C_{3.67}H_{5.41}O_{2.01} + 4.02\ O_2 = 3.67\ CO_2 + 2.71\ H_2O$

Molecular weight: 81.55 128.6

$$\frac{128.6}{81.55} = 1.58 \text{ mg COD per mg extract}$$

*Oxygen assumed to be remaining percentage for the purpose of making the COD calculations.

quality and quantity of organic matter present in ground waters to a defined degree of accuracy. Not all of the organic matter in the water was completely adsorbed on the activated carbon, and not all the organic matter adsorbed on the carbon was extracted with the solvents used. Also, any compounds, which were volative at or below 100°C., may have been lost. Despite all these losses, the fact that the purity of the extracts was not precisely determined, and the possibility that some structural changes might have occurred during the extraction procedures; considerable, consistent, and meaningful quantities of organic matter were obtained from the waters tested. The water at Philo was found to contain about one-third as much organic matter as the other waters studied. This water also contained much less iron and presented no difficulty with iron removal.

Surprisingly, these well waters contain considerably more organic matter than many surface waters presently being studied for organic pollution. These well waters were found to contain 1.5 to 7.3 mg/1 total organic extract while the Missouri River at Saint Louis, Missouri was found by Myrick and Ryckman (106) to contain less than 1.0 mg/1. Mueller, et al. (92) reported that carbon filter samples from the Mississippi and Ohio Rivers revealed from 0.19 to 0.38 mg/1 while low temperatures distillation and extraction with ethyl ether yielded from 1.0 to 2.4 m/1 of organic material. Of this higher figure 33 to 62 percent was nonvolatile. Not all surface waters reported, however, are lower in organic content. Shapiro (60) found the highly colored water of Lower Linsley Pond in Connecticut to contain between 4.5 and 9.0 mg/1 of organic acids. It is

evident that the concentration of organic matter in some well waters is as high as in many surface waters.

C. Effects of Organic Extracts on the Filterability of Iron

After the extracts had been obtained, demonstrating the presence of organic matter in the ground waters under consideration, studies were designed to determine what effects if any these extracts would have on the filterability of iron. In previous work at the University of Illinois by Longley (10), Ghosh (42), and Komolrit (49), studies of the mineral characteristics of waters and oxidation rates of iron in the various waters had revealed no sources of interference with iron removal. In fact, the iron was always found to be in the ferric state when it reached the filters. Because of the low solubility of ferric iron, satisfactory treatment should have been assured in all these waters. It thus seemed that the interference with iron removal was an inability of the iron to form flocculant particles of sufficient size to be retained by rapid sand filters.

As has been discussed previously, it was decided not to measure either chelation capacity or zeta potential, but to measure directly the quantities of iron which could be held in a filterable condition by known amounts of the various extracts. In order to guard against the possibility of side reactions which might give erroneous results, only a minimum of chemicals were added to the test solutions. Sodium hydroxide and hydrochloric acid were used to adjust the pH to 8.0; small quantities of dioxane and potassium chloride were used to dissolve the extracts; distilled water

vas used as the dispersion medium; air was used as the oxidizing agent; 'errous sulfate was used as the ferrous iron source in most experiments, ind ferric nitrate was used when it was desired to add iron already in the erric state. A pH of 8.0 was used as this was close to the pH of the natu-·al waters studied after they had been aerated. When iron first started to ippear on the membrane filters, the pH was raised or lowered in several if the experiments so as to determine the pH dependency of the extracts. ;everal of the extracts were studied after having been put into a strictly vater solution and were found to produce effects slightly greater than when ioxane and potassium chloride were used as the original solvents for the rganic extracts. As it was very difficult to put some of the extracts into olution with water only and as the solvent system was found to give results n the conservative side, the solvent system was used in most of the experi-ients. Air was introduced into the solutions by diffusion and by the vortex roduced by stirring with a magnetic stirrer. There was undoubtedly a light amount of carbonate alkalinity present from the carbon dioxide bsorbed with the oxygen from the air but it did not appear to affect the esults. Although the iron was added as ferrous sulfate, it oxidized so apidly, when it contacted the aerated water at pH 8.0, that it was always npossible to detect ferrous iron in the test solutions even though deter-inations were made immediately after the addition of the iron. Actual gs of these experiments are given in Appendix B. A summary of these esults is given in Table 8. The table lists the maximum concentrations iron found in the filtrates.

EFFECTS OF ORGANIC EXTRACTS ON THE FILTERABILITY OF IRON

Town	Experiment No.	Extract (5 mg/1)	Max. Amount of Iron in Filtrate mg/1	Max. Amount of Iron in Filtrate Due to Extract mg/1	Max. Amount of Iron in Filtrate Due to Extract mg/mg Ext.	Total Extract Obtained from Raw Waters* mg/1	Possible Iron in Sol. Due to Ext. mg/1	Total Possible Iron in Sol. Due to Ext. mg/1
Deland	i	Chloroform A	0.48	0.00	0.00	0.07	0.00	
		Ethanol A	0.42	0.00	0.00	1.00	0.00	0.00
Clinton	ii	Chloroform A	0.12	0.00	0.00	0.01	0.00	
		Ethanol A	1.20	0.64	0.13	0.28	0.04	0.00
Deland	iii	Chloroform A	0.94	0.38	0.08	0.13	0.01	
		Ethanol A	0.30	0.00	0.00	0.57	0.00	0.01
Champaign	v	Chloroform A	0.34	0.00	0.00	0.04	0.00	
		Ethanol A	0.34	0.00	0.00	0.16	0.00	
		Ammonia A	1.90	1.34	0.27	0.16	0.04	0.04
		HCl A	0.00	0.00	0.00	0.66		
Oakwood	1	Chloroform A	0.12	0.00	0.00	0.89	0.00	
		Water A	2.00	1.44	0.29	0.31	0.09	
		Ethanol A	0.40	0.00	0.00	0.30	0.00	
		Ammonia A	0.42	0.00	0.00	0.25	0.00	
		HCl A	0.18	0.00	0.00	1.71		
		Chloroform B	0.32	0.00	0.00	0.87	0.00	
		Water B	2.60	2.04	0.41	0.45	0.18	
		Ethanol B	2.40	1.86	0.37	0.52	0.19	
		Ammonia B	1.52	0.96	0.19	0.41	0.08	0.54
		HCl B	0.32	0.00	0.00	1.13		

* From Table 3 and Table 4

Town	Experiment No.	Extract (5 mg/1	Max. Amount of Iron in Filtrate mg/1	Max. Amount of Iron in Filtrate Due to Extract mg/1	mg/mg Ext.	Total Extract Obtained from Raw Waters* mg/1	Possible Iron in Sol. Due to Ext. mg/1	Total Possible Iron In Sol. Due to Ext. mg/1
Philo	2	Chloroform A	0.12	0.00	0.00	0.06	0.00	
		Water A	0.20	0.00	0.00	0.07	0.00	
		Ethanol A	0.54	0.00	0.00	0.17	0.00	
		Ammonia A	0.14	0.00	0.00	0.13	0.00	
		HCl A	0.16	0.00	0.00	0.68	0.00	
		Chloroform B	0.14	0.00	0.00	0.07	0.00	
		Water B	0.16	0.00	0.00	0.01	0.00	
		Ethanol B	0.48	0.00	0.00	0.77	0.00	
		Ammonia B	0.16	0.00	0.00	0.22	0.00	
		HCl B	0.06	0.00	0.00	0.12		0.00
Clinton	3	Chloroform A	0.16	0.00	0.00	0.04	0.00	
		Water A	None Present					
		Ethanol A	0.46	0.00	0.00	0.12	0.00	
		Ammonia A	1.08	0.52	0.10	0.29	0.03	
		HCl A	0.00	0.00	0.00	2.49		
		Chloroform B	Lost Sample**		0.00	0.30	0.00	
		Water B	Lost Sample**		0.81	0.70	0.57	
		Ethanol B	0.30	0.00	0.00	1.88	0.00	
		Ammonia B	4.64	4.08	0.82	0.42	0.34	0.94
		HCl B	0.32	0.00	0.00	0.60		

** Sample lost, values are from Clinton Run 5.

	Experiment No.	Extract (5 mg/l)	Max. Amount of Iron in Filtrate mg/l	Max. Amount of Iron in Filtrate Due to Extract mg/l	Max. Amount of Iron in Filtrate Due to Extract mg/mg Ext.	Total Extract Obtained from Raw Waters* mg/l	Possible Iron in Sol. Due to Ext. mg/l	Total Possible Iron In Sol. Due to Ext. mg/l
Atwood	4	Chloroform A	0.12	0.00	0.00	0.09	0.00	
		Water A	3.24	2.68	0.54	0.61	0.33	
		Ethanol A	1.04	0.48	0.10	0.43	0.04	
		Ammonia A	0.88	0.22	0.04	0.28	0.01	
		HCl A	0.00	0.00	0.00	1.16		
		Chloroform B	0.28	0.00	0.00	0.25	0.00	
		Water B	4.92	4.36	0.87	1.11	0.97	
		Ethanol B	5.20	4.64	0.93	0.93	0.86	
		Ammonia B	3.84	3.28	0.66	0.87	0.57	2.78
		HCl B	1.00	0.44	0.09	0.41		
Clinton	5	Chloroform A	0.24	0.00	0.00	0.08	0.00	
		Water A	None Present					
		Ethanol A	0.42	0.00	0.00	0.59	0.00	
		Ammonia A	0.70	0.00	0.00	0.46	0.00	
		HCl A	0.00	0.00	0.00	2.09		
		Chloroform B	0.40	0.00	0.00	0.30	0.00	
		Water B	4.60	4.04	0.81	0.68	0.55	
		Ethanol B	5.36	4.80	0.96	1.72	1.65	
		Ammonia B	5.60	5.04	1.01	1.05	1.06	
		HCl B	0.26	0.00	0.00	0.64		
		Chloroform C	0.06	0.00	0.00	0.17	0.00	
		Water C	5.84	5.28	1.06	0.67	0.71	
		Ethanol C	4.28	3.72	0.74	1.00	0.74	
		Ammonia C	3.52	2.96	0.59	0.57	0.34	5.05
		HCl C	1.08	0.52	0.10	0.64		
D Tartaric Acid			24.10	23.50	4.70			
No extract added			0.56	0.56				

The conditions of the tests as reported in Table 8 are as follows:

1. Concentration of organic extract in the test solution is 5.0 mg/l.
2. Dioxane and dilute potassium chloride were used initially to dissolve the extracts.
3. Iron was added as ferrous sulfate in increments as indicated in Appendix B.
4. The pH was 8.0 at the time samples were filtered.
5. Five minutes was allowed for reaction time after iron was added before the samples were filtered.
6. The volume filtered was 35 ml.
7. Membrane filters with a 0.22μ pore diameter were used.
8. The filter diameter was 7/8 inch.
9. Mixing and aeration was with a magnetic stirrer.

It was realized that if the extracts retained very much residual iron through the extraction procedures, any effects, which might have otherwise been attributed to the iron added during the filtration studies, would be masked or at least reduced. Fortunately, however, when the extracts were analyzed for iron, they were found to contain less than one percent iron.

To illustrate the total effect of the extracts on holding iron in solution or suspension, the concentrations of the extracts, as found in the ground waters, are listed in Table 8. These concentrations are used to show the concentrations of iron which could be held in a filterable condition with these amounts of organic matter. Filtration studies, made using ferrous sulfate

without adding any organic extracts, showed that approximately 0.5 mg/l of iron could pass through the filters without assistance from any organic sequestering agents or colloids. It appears that when the iron was present in low concentrations, the hydrated ferric oxide present exhibited little if any tendency to flocculate and thus the particles were small enough to pass through a 0.22μ membrane filter. It is again noted that ferrous iron determinations made on the solution in the reaction vessel always gave negative results even though the determinations were made immediately after adding iron as ferrous sulfate and allowing no more than a minute for mixing. Therefore, the maximum amount of iron in the filtrates which could actually be attributed to the organic extracts was approximately 0.5 mg/l less than the observed amounts. With an adjustment of 0.56 mg/l, many of the extracts exhibited no apparent effect on the filterability of iron.

The effects of the various extracts from a particular water were considered to be additive. This assumption was made as it appeared that the various fractions obtained were not duplications but actually indicated that additional portions of the organic matter present in the water were being extracted with appropriate solvent adjustments. It is further noted that the only extracts which exhibited any significant effects on the filterability of iron were obtained with polar solvents and, as will be shown later, were found to exhibit similar chemical characteristics.

In Appendix B, the actual logs of these experiments, the column headed "Iron on Filter" refers to the membrane filters used. A "-" signifies that no iron precipitate could be detected on the filter. A "$\pm$" means

that a barely detectable yellow precipitate could be seen on the filter. A "+" indicates that a definite yellow to orange precipitate was present on the filter. Finally a "++" designates a very heavy precipitate and that the filter was actually starting to clog. In addition to listing the amounts of iron in the test solutions, the increasing amounts of iron in the filtrates, and the points where iron first appears on the filters; results of increased times of reaction, variations in pH, changes in pore size of the filter paper, and changes in the diameter of the filter paper are listed.

Ferric nitrate was added to several of the extracts in order to observe the amounts of iron which could be held in solution if the iron was already in the ferric state when it was added to the organic extracts. In most cases the maximum amounts of iron found in the filtrates were less than the amounts observed when ferrous sulfate was used as the iron source. This is most probably because the ferric nitrate had had time to undergo sufficient polymerization reactions so that the large ferric hydroxo complex ions thus formed were less subject to being stabilized as colloids or entering into chelation reactions with the organic acids present. Actually this condition probably does not exist in ground waters as the iron is already in contact with the organic matter before and when it is oxidized to the ferric state.

Perhaps the most revealing fact to be gleaned from a study of the logs in Appendix B is that, no matter how much iron an extract was capable of holding in a filterable condition, the addition of sufficient additional iron would cause practically all the iron to be retained by the filters. If the reaction involved was chelation, it would be reasonable to expect the chelating

agents to hold their maximum capacities of iron in solution no matter how much additional iron was added. However, it appears that the organic extracts are either negative colloids or are large molecules in solution which possess sufficiently high negative charges through ionization and Van der Waals forces to physically act as though they were colloids. Thus when iron was first added and oxidized to the ferric state, it was drawn to the negatively charged organic particles and held in colloidal suspension until sufficient iron was added to reduce the zeta potential to a point where the particles could flocculate. It is possible that iron floc first started to appear on the filters only when the zeta potential had been reduced sufficiently to allow some particles to grow sufficiently to be stopped by the membrane filters being used. As more iron was added, coagulation and flocculation became more efficient until almost 100 percent of the iron had formed into particles large enough to be filtered from solution. This size dependency is further demonstrated by the use of the 0.45μ membrane filters instead of the 0.22μ membranes generally used. When membrane filters with the larger pore diameter were used, more iron was required to cause a precipitate to become visible and the maximum amount of iron which could be held in a filterable condition was always greater.

It was always possible to filter a greater concentration of iron through the two inch diameter filter than through the 7/8 inch diameter filter. It appears reasonable that when the zeta potential had been reduced sufficiently so that some particles were beginning to build to sufficient size to be retained by the filter medium or pore diameter, the particles which

lodged on the filter surface not only tended to partially block the filter passages but smaller particles in the solution being filtered were forced into close proximity with the larger particles and the flocculation tendency was increased. Thus under such conditions when flocculation was just beginning, the smaller the surface area of the filter, the greater was the tendency for particles to build up in a greater density and increase the flocculation forces on the remainder of the solution.

When additional reaction time was allowed prior to filtration, very little difference was noted in the filterability of the iron. This would seem to indicate that the dispersions were formed fairly rapidly and their stability was not affected by time.

Changes in pH provided other evidence that the holding of iron in a filterable condition was caused by colloidal dispersion. When iron began to appear on the filter membranes, a higher concentration of iron was held in a filterable condition if the pH of the solution was raised from 8.0 to 9.0. If the pH was lowered from 8.0 to 6.0, a greater portion of the iron was retained by the filter. Thus it appears that as more hydroxyl ions became available to enter the double layer surrounding the colloids, the greater became the negative zeta potential. Although this is another demonstration of the possibility that the interference is colloidal, pH dependence does not rule out the possibility of chelation as organic chelating agents can increase and decrease in chelation capacity as ionization of carboxyl groups at increasing pH values makes them more readily available as chelation sites.

This work substantiates and further explains some of the observa-tions made by Shapiro (60, 78, 79, 90) if it can be concluded that the extracts obtained from ground waters were similar in character to those from the surface waters studied by Shapiro. Although much more thorough character-izations have been made of the surface water extracts, all results obtained in characterizing the ground waters have been in agreement with the surface water analyses. These analyses will be discussed more fully in the next section. Also the iron filteration studies seem to be in substantial agree-ment at all points of comparison.

Shapiro found that most of the extracts were dialyzable through a cellophane membrane and thus not colloidal. He, however, found that, when iron was added to his extracts, it was held in a filterable condition when fil-tered through 0.45 and 0.22μ membrane filters, but this iron was not fil-terable through 0.10μ filters. Filterability of iron with the ground water extracts was not tested through 0.10μ filters but the other observations hold true. Shapiro suggested that the iron had been peptized in a colloidal state. He further demonstrated this colloidal condition by adding electrolytes such as potassium chloride and aluminum chloride and found that they were cap-able of destabilizing the iron colloids. Thus it would appear that the main-tenance of large quantities of iron in suspension is caused by organic compounds with the capacity to stabilize colloidal dispersions. When the filtration studies were being made, it was noticed that 5 mg/1 of the extracts did not produce a color detectible by the human eye but the addition of as little as 0.2 mg/1 of iron quickly produced a definite yellow color which

increased in intensity as more iron was added. This color was more intense than the color which would be caused by iron alone and appeared similar to the color imparted to water from decaying vegetable matter. It is thus quite possible that the humic acids in surface and ground waters have the same source and are similar to the humic acids in soils.

D. Characterization of the Organic Extracts

One characterization of the organic extracts was, of course, the measurement of their ability to hold iron in a filterable condition. The solvent system described by Mueller, et al. (92) to identify dicarboxylic acids with ascending paper chromatographs was attempted with several of the extracts. Three of the five extracts spotted were acidic enough to react with methylene blue, which was used to develop the chromatograph, to form yellow spots which indicated their final locations on the chromatograph. The "Rf" values of these extracts, or the ratio of movement of the extracts to the movement of the solvent front, were compared with several known acids. Only one of the extracts was found to move while all the acids tested ascended the paper and produced distinct spots with the exception of oxalic acid which produced a streak. The chromatograph is reproduced to scale in Figure 9. In Table 9 are tabulated the compounds and their Rf values.

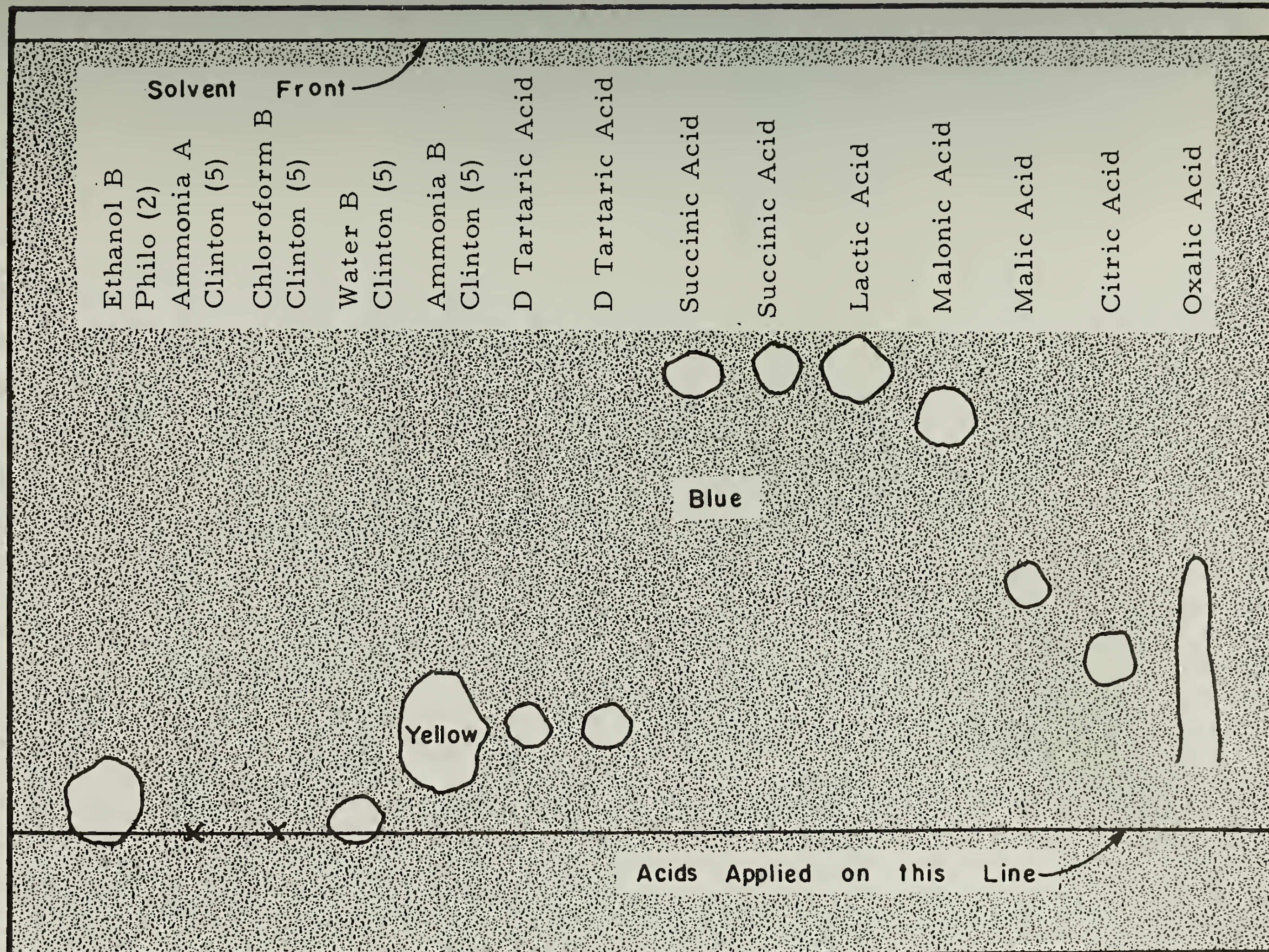

FIGURE 9

ASCENDING PAPER CHROMATOGRAPH

TABLE 9

PAPER CHROMATOGRAPH OF ORGANIC ACIDS

Acid or Extract	Town	Experiment Number	Rf Values
Ethanol B	Philo	2	0.03
Ammonia A	Clinton	5	*
Chloroform B	Clinton	5	*
Water B	Clinton	5	0.02
Ammonia B	Clinton	5	0.13
D Tartaric Acid			0.14
D Tartaric Acid			0.14
Succinic Acid			0.59
Succinic Acid			0.61
Lactic Acid			0.61
Malonic Acid			0.54
Malic Acid			0.32
Citric Acid			0.23
Oxalic Acid	(To top of streak)		0.31

*Final location not visible on developed chromatograph.

This test indicates that three of the five extracts were of sufficient acidity to be detectable in the determination. Also there is a possible indication that tartaric acid might be present in the ethanol plus ammonia extract from the acidified filter at Clinton. These extracts had possibly not been purified sufficiently to give satisfactory results with paper chromatography. Even the possible presence of the acids as their metal salts could interfere with the results. Also there was no assurance that the reference acids used covered even a small portion of the acids which could possibly be present in the extracts. However, this brief attempt does demonstrate that paper chromatography can be a useful tool in the more complete analysis of organic acids present in ground water.

A more definite characterization of several of the extracts was

made using infra-red spectroscopy. The spectra are reproduced in Appendix C. The spectra are essentially the same whether the extracts were scanned as smears on sodium chloride crystals or molded into potassium bromide pellets. As the extracts had not undergone extensive purification prior to making these analyses, several undefined peaks appear on several of the spectra. Bellamy (101) has listed the wavenumbers in cm^{-1} of the carboxylic acids to have one or two peaks between 3500 and 2500 cm^{-1} and two other peaks in the region between 1725 and 1300 cm^{-1}. Spectra from the Sadtler Research Laboratories (107) were used to determine the spectrum of distilled water which can mask spectra in samples which are not completely dry. Major peaks are found at 3400 and 1650 cm^{-1}. Thus these peaks can mask the appearance of peaks from carboxylic acids.

Of major interest is the fact that most of the extracts show definite peaks in the characteristic regions for carboxylic acids. This is in close agreement with Shapiro (60, 78, 79, 90) and Rice, et al. (102) who found organic acids in surface waters to have similar infra-red spectra. Frisch and Kunin (108) found the organic foulant, from anion-exchange resin used to treat Delaware River water at Philadelphia, produced a similar spectrum indicating organic acids. They also found that tea and an infusion made from leaves produced a similar spectrum, indicating the probable origin of all these organic acids and that these acids are "humic acids" or decomposition products from decaying vegetable matter.

Puri and Sarup (93) reported that humic acids usually show an equivalence, when titrated with a strong base, at about pH 7. 5. Also humic acids

were reported to demonstrate titration curve equivalence points about 4 pH units above the original pH values of the acids in distilled water. In Figure 10 are reproduced the titration curves for several of the extracts. All the extracts obtained with polar solvents show just such characteristic curves which further demonstrate the likelihood that these extracts are "humic acids." Tartaric acid and the chloroform extract titrated did not show the same leveling off of pH above the equivalence point as did the other extracts. As the ionizable hydrogen ions, from both carboxyl groups in tartaric acid, are both given off below pH 5, it and the chloroform extract, which is likely to be highly non-polar, show no further effect on the titration curves and the pH continues to rise just as it would if the strong base was added to distilled water.

In Appendix B are listed the initial pH values of the test solutions used in the filtration study. These pH measurements were made on the test solutions prior to pH adjustments or the addition of any iron. Although they offer no quantitative information, the fairly close agreement of these values seems to indicate that the functional groups of all the extracts have been subjected to similar pH influences during the extraction procedures.

Using the method described by Middleton (81), attempts were made to identify several of the extracts from Clinton Experiment 5 by solvent separations. As had been expected, the polar water-soluble extracts exhibited very little solubility in the non-polar solvent, ethyl ether. In Table 10 are given the results of these separations.

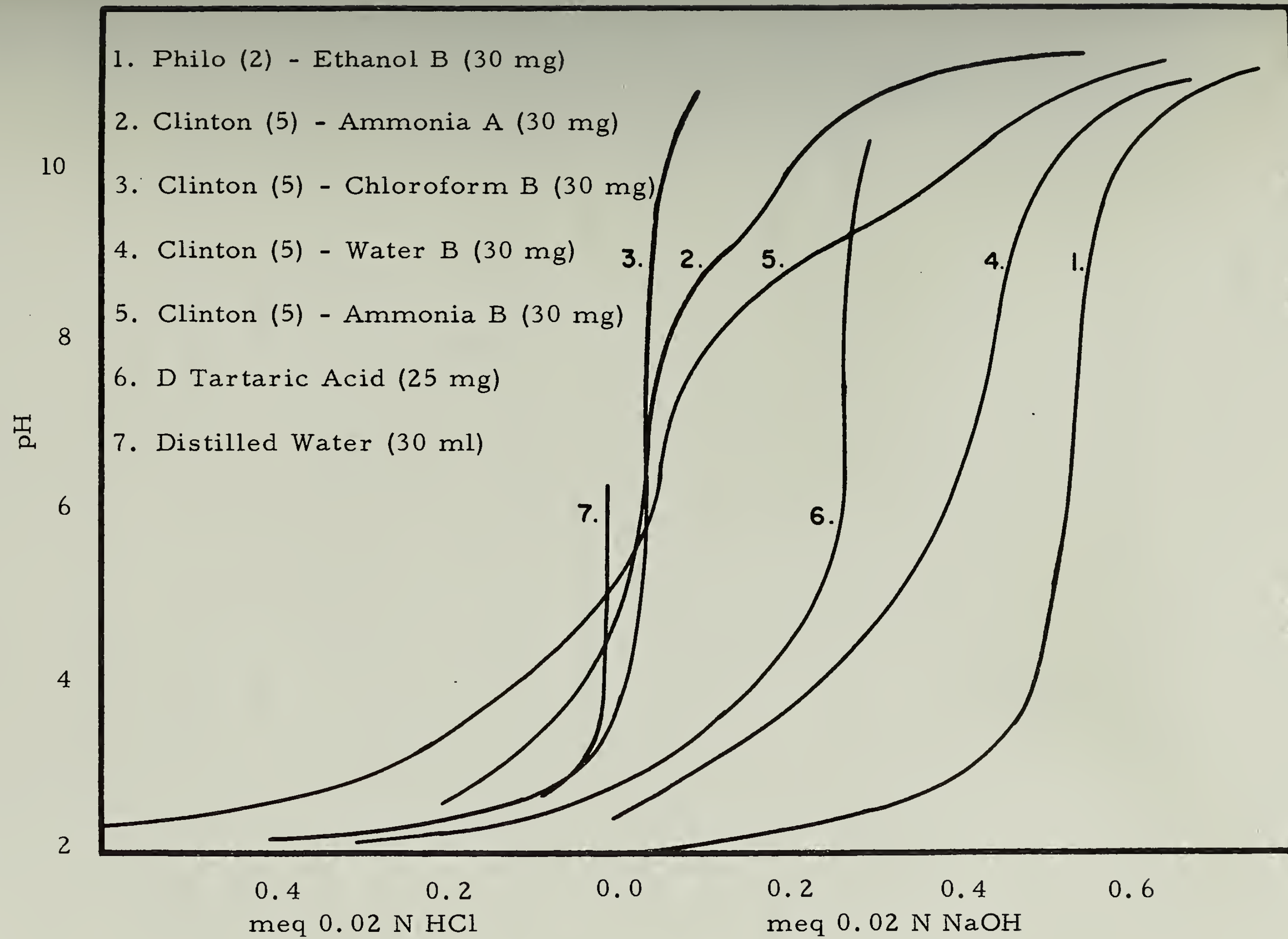

FIGURE 10

TITRATION CURVES FOR ORGANIC EXTRACTS

TABLE 10

SOLVENT SEPARATION OF ORGANIC EXTRACTS

Clinton - Experiment Number 5

Extract	Ether Soluble Percent
Ammonia	6.25
Water B	0.93
Ammonia B	7.45
Chloroform B	67.05

The results of the solvent separation study, the results of the titration study, the tentative identification of carboxyl groups by infra-red spectroscopy, and the fact that several of the extracts possessed sufficient acidity to produce acid reactions on the paper chromatograph, provide a reasonable indication that organic acids are present in the ground waters studied and were obtained as extracts when polar solvents were used. The extracts had a physical appearance similar to the extracts described by Shapiro (60, 78, 79, 90) and Rice, et al. (102). The extracts were a deep orange to brown color, very hard and brittle, but they chipped off easily from the walls of the drying flasks and were ground to a dark brown powder which gave off a characteristic burnt sugar odor. Shapiro (60) suggested a molecular structure for the extracts from surface waters of $(C_{50}H_{62}0_{27}N)_n$ or $C_{21}H_{26}O_{11}$. The average molecular weight was found to be 456 and the equivalent weight was found to be exactly one-half the molecular weight or 228, indicating two ionizable acid groups per molecule. Although no attempt has been made to determine the molecular weight of the extracts from ground water, it is quite possible that the findings would be similar.

E. Field Study of the Effects of Organic Extracts on Iron Removal

After the extracts had been obtained from the well waters and had been shown to interfere with the satisfactory filtration of iron in the laboratory, it was still necessary to see if these same extracts could be made to cause an interference with filtration of iron from natural water. Although the extracts had shown no retarding effect on the rate of oxidation of ferrous iron in the laboratory, the fate of ferrous iron was observed in the field tests and compared to similar samples which did not contain organic extracts. In addition to observing oxidation, a comparison was made of the filterability of iron with and without the addition of organic extracts.

Field studies were made at Philo, and Clinton, but no study was made at Oakwood because a preliminary oxidation test showed the iron in Oakwood well water to be completely oxidized within two to three minutes after air was added. This time interval was too short to allow for adequate observations. Studies were also made at Atwood with the results having been previously reported by Marsh (43). For the waters studied, a sample was drawn without aeration. Dissolved oxygen (which was always practically nil), ferrous iron, total iron, pH, and temperature were measured. At this point, if a particular organic extract was to be studied, it was added, the sample was aerated, and then the rate of change of filterability and the rate of ferrous iron oxidation were observed.

Figure 11 is a graphical representation of the rate of oxidation of iron to the ferric state and the rate of change of the iron from a filterable to a nonfilterable condition. This study was made at Well No. 4 at Philo

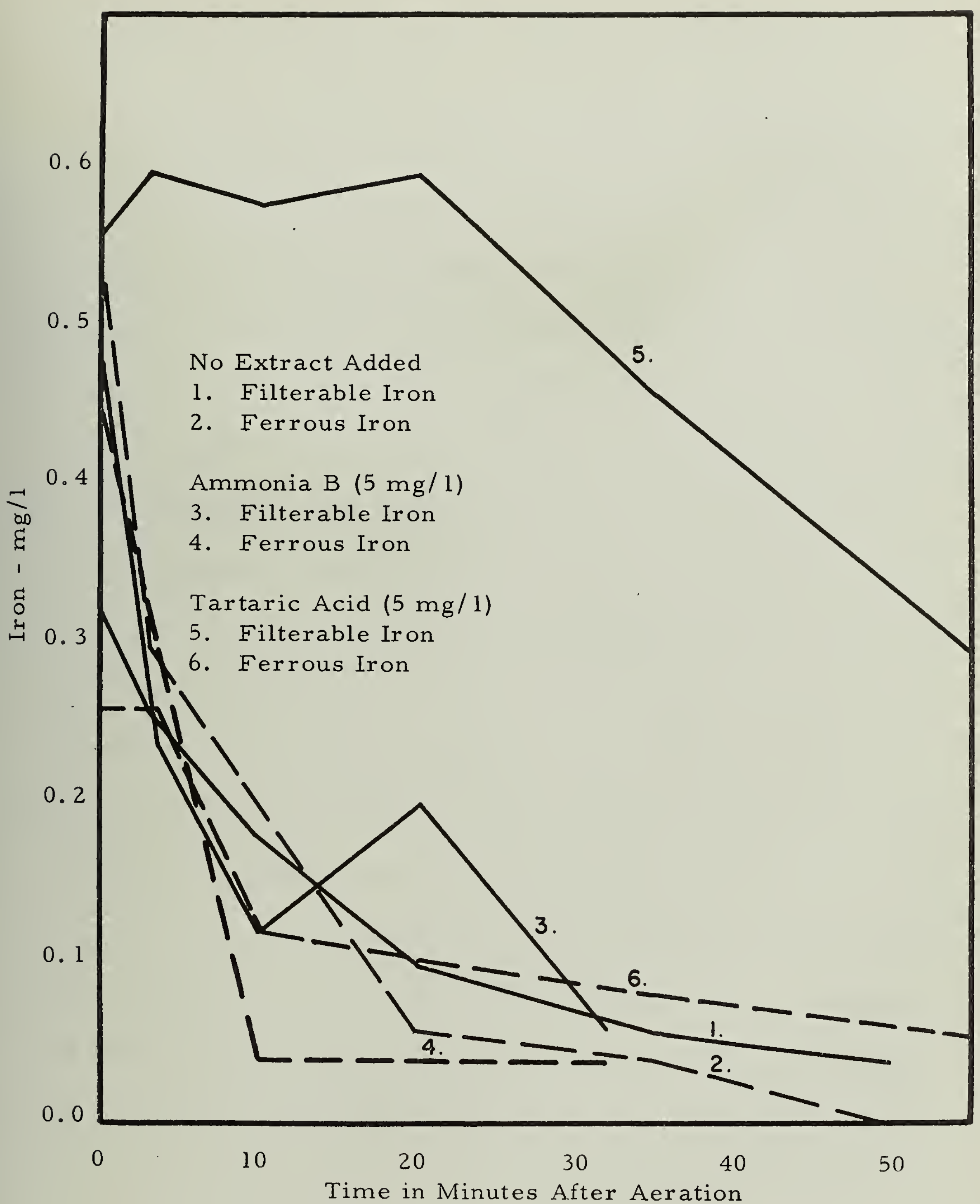

FIGURE 11
IRON OXIDATION AND FILTRATION STUDY
AT PHILO, ILLINOIS

because at the time of the study there was insufficient iron present in the water from Well Number 3 to make the necessary observations possible. Experiments were made using the ethanol plus ammonia extract from the acidified filter used at Philo Well Number 3, using tartaric acid, and, as a control, using a sample to which no extract had been added. A similar graph for a study made at Clinton is given in Figure 12. In most tests 5 mg/l of extract was added but in one of these tests 50 mg/l of extract was added to see if an interference could be detected with this increased concentration. The logs of these tests are given in Appendix D. All the studies produced similar results. Neither the extracts nor tartaric acid produced any noticeable change in the normal oxidation rate of iron for these waters. This would seem to indicate that the presence of organic matter in water has little bearing on the rate of oxidation of iron to the ferric state. Tartaric acid did measurably, but not greatly, retard the conversion of iron to a nonfilterable condition, whereas the extracts exhibited no measurable influence on the filterability of iron. Tartaric acid in the laboratory tests also showed a much higher capacity for holding iron in a filterable condition. Thus, it appears that organic matter in water could possibly have some influence on the rate of change of iron from a filterable to a nonfilterable condition; however, this influence seems to be so slight as to be of no consequence for the concentrations of organic matter normally present in ground waters.

These tests were extended by March (43) to a study of all extracts available for the water from Atwood and from Clinton. He noted that the change from ferrous to ferric iron was more rapid than the change from

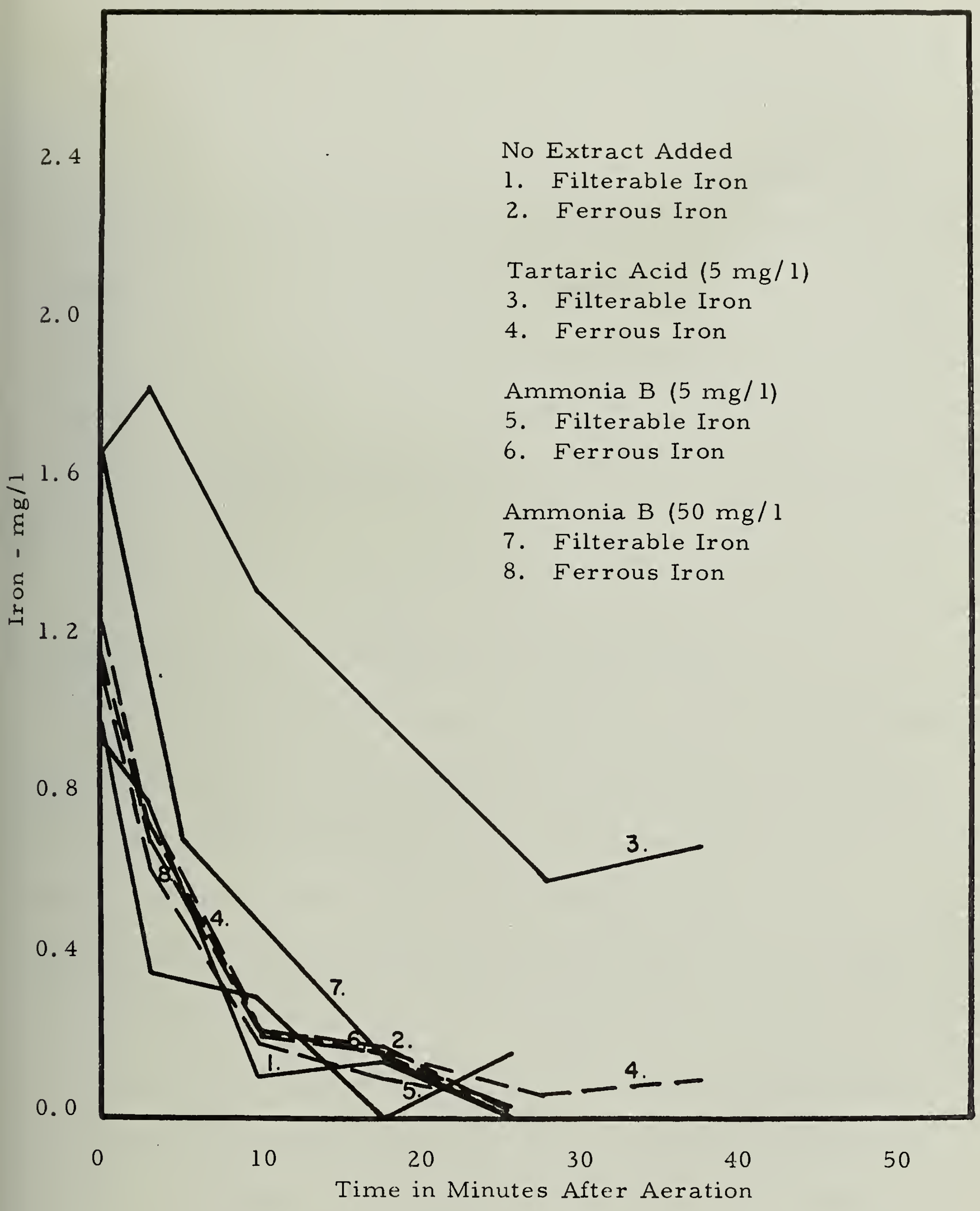

FIGURE 12
IRON OXIDATION AND FILTRATION STUDY
AT CLINTON, ILLINOIS

a filterable to a nonfilterable condition. This is the same phenomenon observed in the laboratory study when a gradual increase in the iron remaining on the filter paper catalyzed the precipitation of the remaining iron.

The rates of oxidation of the iron were considerably higher than those predicted by the equation proposed by Ghosh (42). The calculated time for the oxidation of one-half of the iron was 78 minutes for Philo and 27 minutes for Clinton while in both cases more than one-half the iron was oxidized in less than 10 minutes. It is to be noted, however, that the water at Philo had a much lower alkalinity than the range covered in the determinations by Ghosh.

F. Proposed Source of the Interference with Iron Removal

None of the field studies revealed any interference with iron removal by oxidation and filtration. This occurred even though the extracts added to the waters had shown the ability to retain iron in a filterable condition in the laboratory, and these same waters had been previously reported to exhibit inadequate iron removal with just the organic concentration present in the natural waters. The laboratory determinations demonstrated that the normal concentrations of organic matter present in all the waters studied, except the water at Philo, were sufficient to hold significant quantities of iron in a filterable condition. Yet in none of these studies, the studies by Marsh (43), or the studies by Longley (10) was it ever possible to filter a water through any type of pilot plant filter without obtaining at least 99 percent iron removal.

There seems to be only one explanation remaining for the interfer-
erence with iron removal for the waters studied. The waters, which were
ound to contain considerable concentrations of organic matter, were the
vaters which had exhibited the most unsatisfactory iron removal in actual
lant operation. Thus it appears that the interference with iron removal
s due to the presence of organic matter but, as previous discussion in
his study has demonstrated, the interference is apparently not interfer-
nce with filtration by colloid stabilization or chelate formation.

Holluta and Eberhardt (109) in a study of iron filtration found that
ll of the iron passing through a sand filter was in the ferrous state in
he filter effluent. Komolrit (49), in a study of the efficiency of operation
f iron removal plants for several Illinois ground waters, found that, when
here was iron in a finished water, the major portion of the iron passing
hrough the filter was in the ferrous state as it left the filter. It seems
hen that the problem is not one of chelation or colloidal dispersion but
ne of reconversion of the iron back into the soluble ferrous form.

Komolrit also observed that the plants experiencing trouble with
ron removal were also showing much less dissolved oxygen in the finished
ater than in the water as it was applied to the filters. The waters in
linois which were difficult to treat also were observed to present problems
ith persistent slime growths on top of the filter media. This then sug-
ests that the interference is actually biological reduction of the iron as
part of the metabolism of bacteria or other simple organisms which are
sing the humic acids present as a food source. This prevalence of slime

ınd the reducing conditions present, as indicated by the reduction of iron ınd dissolved iron concentration, seem to tie together. In the Netherlands 26) it was found that by using dry filtration, i. e. holding the water surace always just below the surface of the filter sand, iron filtration was ılways satisfactory. This and Mathews' findings (16) that break-point :hlorination insures satisfactory iron removal both indicate the possibilty that the prevention of the formation of a slime growth can insure satisactory iron removal.

V. CONCLUSIONS

1. Carbon filters can satisfactorily be used to extract organic matter from ground water. However, in order to insure adequate extraction of particular fractions of interest, proper solvents and pH must be used. The three inch diameter by eighteen inch standard carbon filter will produce satisfactory reproducible results at an application rate of one gallon per minute or at about four times the application rate normally recommended. Two filters in series, with the water acidified before it is applied to the second filter, will produce at least twice the extract as the unacidified filter alone. Although the carbon filter cannot be expected to provide an absolute measure of the quantity of organic matter present in a well water, the filter does provide for the extraction of meaningful quantities.

2. Organic extracts can be obtained from ground waters in a condition reasonably separated from the inorganic constituents present in the water by the carbon filter technique.

3. At least some ground waters contain significant quantities of organic matter. Most of this organic matter is soluble in polar solvents. The extracts, obtained from the Illinois ground waters studied, exhibited color, odor, titration, and infra-red spectrum characteristics of the humic acids or acids formed during the decomposition of vegetable matter.

4. Most of these extracts can hold iron in a filterable condition in laboratory tests in alkaline conditions but upon the addition of sufficient excess iron, all the iron is retained by filtration. This indicates that the

organic matter creates colloidal dispersions and not soluble chelates.

5. Although the extracts obtained from the waters under consideration were able to maintain the iron in a filterable condition in laboratory tests, field tests were never able to reproduce this phenomenon. It is hypothesized that the actual interference with iron removal is biological activity, supported by the humic acids in the well water, creating reducing conditions in a slime layer at the surface of or within the filters. These reducing conditions may reconvert the iron to the soluble ferrous form.

6. The organic extracts obtained did not interfere with oxidation of ferrous iron to the ferric state.

7. The organic acids found in the ground water are similar to the humic acids found in soils and in surface waters.

8. The ground waters considered in this study, which demonstrated difficulties with iron removal, were all found to contain significant amounts of organic matter. This, and the fact that organic extracts from these waters can hold iron in a filterable condition at least in laboratory studies, indicates the possibility that organic acids are at least partially responsible for the solution and transport of iron in ground water.

VI. AREAS OF FUTURE STUDY

1. A study should be made of the bacteria present in rapid sand ilters in an attempt to demonstrate their ability to cause reduction of iron n filters.

2. If this is found to be the case, then a search should be made for satisfactory method to control slime growth.

3. A study should be undertaken to further classify and actually dentify the various organic compounds present in ground water. This hould be undertaken, not only from the standpoint of interference with ron removal, but also to establish methodology for monitoring ground ater for possible pollution by intrusion of such things as insecticides and ther industrial pollutants.

4. This study should be extended to other areas of the United States) see if similar correlations exist generally in all areas with iron removal roblems.

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APPENDIX A

CHEMICAL ANALYSES

. Total Iron

Total iron was determined by the Phenanthroline* Method described n Standard Methods (103). A Beckman Model DU Spectrometer was used o measure transmittance at 512 mμ with a 1.0 cm light path. To insure hat a sufficient amount of 1, 10-phenanthroline was present in samples vith high iron concentrations, 10 ml of the phananthroline solution was dded to the samples instead of the recommended 2.0 ml. When measuring percent iron in the dry extracts, the samples were ashed as per tandard Methods prior to color development.

. Ferrous Iron

The method described by Lee and Stumm (110) of measuring ferous iron using bathophenanthroline was used for this determination. he method is as follows:

a. Reagents

(1). Bathophenanthroline*, 0.001 M solution. The solution was prepared by dissolving 0.0332 gm of 4,7-diphenyl-1, 10-phenanthroline in 50 ml of reagent grade absolute ethanol and diluting to 100 ml with distilled water.

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*Both Phenanthroline and Bathophenanthroline are products of the G. Frederich Smith Chemical Company, Columbus, Ohio.

(2). Extracting alcohol. Reagent grade isoamyl alcohol was used.

(3). Diluting alcohol. Reagent grade absolute ethanol was used.

(4). Sodium acetate, 10 percent solution. The solution was prepared by dissolving 10 gm of sodium acetate in 100 ml of distilled water.

(5). Standard iron solution. A solution made of 20 ml of concentrated sulfuric acid added to 50 ml of distilled water was used to dissolve 0.7022 gm of ferrous ammonium sulfate ($Fe(NH_4)_2 (SO_4)_2 \cdot 6H_2O$). This was then diluted to 1000 ml. Appropriate dilutions were made to establish a standard curve.

b. Procedure for the determination of ferrous iron

(1). A 5 to 15 ml sample was pipetted into a 125 ml separatory funnel.

(2). Then 4 ml of sodium acetate solution was added to the sample.

(3). This was followed by 15 ml of bathophenanthroline after which the sample was swirled gently.

(4). Then 10 ml of the isoamyl alcohol was added. The funnel was shaken vigorously and let stand.

(5). After the phases had separated, the lower aqueous layer was discarded and the colored upper fraction

was transferred to a 50 ml volumetric flask.

(6). The separatory funnel was washed thoroughly with absolute ethanol and the washings were transferred to the volumetric flask. The sample was then diluted to 50 ml with absolute ethanol.

(7). A reagent blank was prepared using 10 ml of distilled water instead of a sample.

(8). The intensity of color developed was measured with a Beckman Model DU Spectrometer at a wavelength of 533 mμ and using a 1.0 cm light path.

3. Dissolved Oxygen

Dissolved oxygen was measured by the Alsterberg (Azide) Modification of the Winkler Method as described in Standard Methods (103).

4. Hardness

Hardness was determined by titration with ethylenediamine tetraacetic acid (EDTA) as per Standard Methods (103). However, instead of using the reagents and inhibitors described, the prepared reagents CalVer II and UniVer II* were used. UniVer II was used for determining total hardness and CalVer II and 1 ml of 8 N potassium hydroxide were used for determining calcium hardness.

* Both CalVer II and UniVer II are products of the Hach Chemical Company, Ames, Iowa.

. Chloride

The mercuric nitrate method described in Standard Methods (103) /as used for determining chloride concentrations.

. Alkalinity

Alkalinity was determined by titration with dilute sulfuric acid as escribed in Standard Methods (103). The end points of the alkalinity itrations were detected with pH meters. The pH meters were standard-zed with pH 4.01 buffer made from Beckman buffer powders*.

. Chemical Oxygen Demand

Chemical oxygen demand (COD) was measured in accordance with tandard Methods (103). For all natural waters the 0.1 dilution method 'as followed and for the extracts the undiluted method was used. Silver ulfate was used as a catalyst in all cases.

Beckman Instruments, Inc., Fullerton, California.

APPENDIX B

LOG OF FILTERABILITY STUDY

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Deland - Experiment i						
Chloroform A	6.80	8.0	0.29	-	0.29	
		8.0	1.10	+	0.48	
Ethanol A	6.80	8.0	0.30	-	0.30	
		8.0	1.10	+	0.42	
Clinton - Experiment ii						
Chloroform A	7.35	8.0	0.20	+	0.12	
Ethanol A	7.00	8.0	0.28	-	0.16	
		8.0	1.20	-	1.20	
		8.0	2.12	+	0.04	
Deland - Experiment iii						
Chloroform A	7.05	8.0	0.21	-	0.21	
		8.0	1.12	-	0.94	
		8.0	1.96	+	0.14	
Ethanol A	6.80	8.0	0.30	-	0.30	
		8.0	1.04	+	0.0	
Champaign - Experiment v						
Chloroform A	6.90	8.0	0.34	+	0.34	
Ethanol A	8.30	8.0	0.34	+	0.34	
Ammonia A	7.80	8.0	0.20	-	. . .	
		8.0	1.00	-	. . .	
		8.0	1.70	-	1.70	
		8.0	2.00	+	1.90	
HCl A	8.10	8.0	0.20	+	0.0	

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Oakwood - Experiment 1						
Chloroform A	7.55	8.0	0.20	+	0.12	
Water A	7.30	8.0	0.50	-	. . .	
		8.0	1.00	-	. . .	
		8.0	2.10	±	2.00	
		8.0	2.40	+	1.60	
		6.9	2.40	+	1.60	pH lowered
Water A	7.30	8.0	1.60	+	1.52	Ferric iron used.
Ethanol A	7.50	8.0	0.40	-	0.40	
		8.0	0.50	+	0.22	
		7.0	0.50	+	0.10	pH lowered
Ethanol A	7.50	8.0	0.20	-	. . .	Ferric iron used
		8.0	0.96	+	0.10	
Ammonia A	7.40	8.0	0.20	-	. . .	
		8.0	0.50	-	. . .	
		8.0	0.88	+	0.42	
		7.0	0.88	+	0.32	pH lowered
Ammonia A	7.40	8.0	0.60	±	0.56	Ferric iron used
HCl A	7.50	8.0	0.36	+	0.04	
		7.0	0.36	+	0.18	pH lowered
HCl A	7.50	8.0	0.20	+	0.14	Ferric iron used
Chloroform B	7.35	8.0	0.32	+	0.32	
Chloroform B	7.35	8.0	0.28	+	0.16	Ferric iron used
Water B	6.55	8.0	1.00	-	. . .	
		8.0	1.40	-	. . .	
		8.0	2.00	-	1.88	
		8.0	2.50	±	2.44	
		8.0	2.72	+	2.60	
		7.0	2.72	++	2.48	pH lowered

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Oakwood - Experiment 1 (Continued)						
Ethanol B	6.55	8.0	1.00	-	. . .	
		8.0	2.20	-	2.12	
		8.0	2.48	±	2.40	
		7.0	2.48	+	2.40	pH lowered
		9.0	2.48	±	2.40	pH raised
Ethanol B	6.55	8.0	2.00	+	1.40	Ferric iron used
Ammonia B	7.30	8.0	1.00	-	. . . .	
		8.0	2.00	+	1.52	
		7.0	2.00	++	0.98	pH lowered
Ammonia B	7.30	8.0	1.74	±	1.64	Ferric iron
		8.0	2.24	+	0.80	used
HCl B	7.00	8.3	0.40	±	0.32	
		8.1	0.50	+	0.10	
		9.0	0.50	+	0.26	pH raised
		7.0	0.50	+	0.08	pH lowered
HCl B	7.00	8.0	0.40	±	0.28	Ferric iron used
Philo - Experiment 2						
Chloroform A	7.50	8.0	0.20	+	0.12	
Water A	7.60	8.1	0.28	+	0.20	
Ethanol A	7.60	8.0	0.34	+	0.54	
Ammonia A	7.60	8.1	0.28	+	0.14	
HCl A	7.60	8.1	0.22	+	0.16	
Chloroform B	7.50	8.0	0.28	+	0.14	
Water B	5.50	8.1	0.40	+	0.16	
		6.0	0.40	+	0.04	pH lowered
		9.0	0.40	+	0.24	pH raised

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Philo - Experiment 2 (continued)						
Water B	5.50	8.1	0.40	+	0.10	Ferric iron used
Ethanol B	6.90	8.1	0.30	±	0.26	
		8.1	0.50	±	0.48	
		8.1	0.60	+	0.48	
		6.8	0.60	+	0.12	pH lowered
Ethanol B	6.90	8.0	0.40	±	0.34	
		8.0	0.64	+	0.04	Ferric iron used
Ammonia B	7.50	8.0	0.32	+	0.16	
		6.0	0.32	+	0.14	pH lowered
Ammonia B	7.50	8.0	0.32	+	0.32	Ferric iron used
HCl B	7.60	8.0	0.30	+	0.06	
Clinton - Experiment 3						
Chloroform A	6.45	8.0	0.23	+	0.16	
		8.0	1.00	+	0.0	
Water A - None present						
Ethanol A	6.70	8.0	0.27	-	0.24	
		8.0	1.00	+	0.46	
		8.0	2.16	++	0.12	
Ammonia A	6.75	8.0	0.16	-	0.08	
		8.0	1.08	-	1.08	
		8.0	2.10	+	0.80	
		8.0	3.16	++	0.12	
HCl A	6.55	8.0	0.28	+	0.0	
Chloroform B - Lost						
Water B - Lost						

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Clinton - Experiment 3 (continued)						
Ethanol B	6.75	8.0	0.26	±	0.30	
		8.0	1.06	+	0.0	
Ethanol B	6.75	8.0	0.31	±	0.16	Repetition
		8.0	1.14	+	0.24	
Ammonia B	6.80	8.0	0.30	-	0.34	
		8.0	1.06	-	0.88	
		8.0	2.02	-	2.00	
		8.0	3.16	-	2.88	
		8.0	4.76	+	4.64	
		8.0	6.14	++	4.32	
Ammonia B	7.10	8.0	0.40	-	0.42	Repetition
		8.0	1.24	-	1.16	
		8.0	2.08	-	2.36	
		8.0	3.00	±	3.08	
		8.0	3.00	+	2.92	10 min. mix before filtering
		8.0	3.92	+	2.28	
		8.0	4.82	++	0.28	
Ammonia B	7.10	8.0	3.32	-	3.20	
		8.0	3.32	-	3.32	24 hrs. reaction before filtering
Ammonia B	6.70	8.0	0.40	-	0.38	Equivalent amount of extract but not heated at 100°C - still liquid
		8.0	1.10	-	1.00	
		8.0	2.10	-	2.12	
		8.0	2.98	-	2.88	
		8.0	4.26	±	4.04	
		8.0	5.52	+	4.32	
HCl B	7.00	8.0	0.22	-	0.24	
		8.0	1.02	+	0.12	
HCl B	7.00	8.0	0.36	+	0.04	Repetition
		8.0	1.14	+	0.32	

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/1	Special Conditions
Atwood - Experiment 4						
Chloroform A	7.50	8.0	0.20	+	0.12	
Water A	6.85	8.0	0.20	-	0.28	
		8.0	0.50	-	. . .	
		8.0	1.00	-	. . .	
		8.0	2.00	-	. . .	
		8.0	3.00	-	. . .	
		8.0	3.50	-	3.12	
		8.0	4.00	+	3.24	
Ethanol A	6.80	8.0	0.30	-	0.24	
		8.0	1.04	+	0.76	
		9.0	1.04	±	1.04	pH raised
		6.0	1.04	+	0.60	pH lowered
Ethanol A	6.80	8.0	0.60	-	0.60	Ferric iron
		8.0	1.00	+	0.04	used
Ammonia A	6.30	8.0	0.20	=	0.22	
		8.0	0.88	+	0.80	
		9.0	0.88	-	0.88	pH raised
		6.0	0.88	+	0.02	pH lowered
Ammonia A	6.30	8.0	0.80	+	0.04	Ferric iron used
		8.0	0.80	+	0.08	0.45μ filter
HCl A	6.50	8.0	0.20	+	0.0	
Chloroform B	7.30	8.0	0.30	+	0.28	
Water B	6.40	8.0	0.20	-	0.20	0.45μ filter
		8.0	1.00	-	. . .	0.45μ filter
		8.0	2.00	-	. . .	0.45μ filter
		8.0	3.00	-	. . .	0.45μ filter
		8.0	4.00	-	. . .	0.45μ filter
		8.0	5.00	-	. . .	0.45μ filter
		8.0	6.00	++	0.56	0.45μ filter
		8.0	6.00	++	0.46	0.22μ filter

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Atwood - Experiment 4 (continued)						
Water B	6.40	8.1	5.00	-	. . .	Repetition
		8.0	5.52	+	4.92	
		7.0	5.52	++	2.84	pH lowered
Water B	6.40	8.2	0.50	-	0.60	Repetition
		8.1	1.00	-	0.92	
		8.1	4.56	±	4.48	
		8.1	4.56	-	4.48	0.45μ filter
		8.2	5.20	-	5.20	0.45μ filter
		8.2	5.20	+	4.88	0.22μ filter
		8.2	5.92	-	5.88	0.45μ filter
		8.2	5.92	-	5.92	0.45μ filter 72 hrs. reaction before filtering
Water B	5.90	8.0	0.31	-	0.34	Repetition
		8.0	1.12	-	1.04	
		8.0	4.04	-	4.00	
		8.0	4.90	+	4.60	
		8.0	6.24	++	1.92	
		8.0	7.60	++	0.32	
Water B	5.90	8.0	0.31	-	0.30	Same series as above but with 2 in. dia. filters
		8.0	1.12	-	1.10	
		8.0	4.04	-	4.00	
		8.0	4.90	-	4.78	
		8.0	6.24	+	5.52	
		8.0	7.60	++	1.26	
Water B	5.90	7.0	0.18	-	0.12	pH lowered
		7.0	1.46	-	1.48	
		7.0	2.00	-	1.92	
		7.0	4.08	-	4.04	
		7.0	5.70	++	0.04	
Water B	5.90	7.0	0.18	-	0.17	Same series as above but with 2 in. dia. filters.
		7.0	1.46	-	1.52	
		7.0	2.00	-	1.92	
		7.0	4.08	-	. . .	
		7.0	5.70	++	0.30	

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Atwood - Experiment 4 (continued)						
Water B	5.60	8.0	0.28	-	. . .	Ferric iron
		8.0	1.08	-	0.92	used
		8.0	2.16	±	2.12	
		8.0	3.12	+	1.52	
		8.0	4.84	++	0.40	
Water B	5.60	8.0	0.28	-	0.26	Same series
		8.0	1.08	-	1.00	as above but
		8.0	2.16	-	2.10	with 2 in.
		8.0	3.12	+	2.84	dia. filters
		8.0	4.84	++	0.76	
Water B	6.90	8.0	0.40	-	0.34	Water used as
		8.0	1.02	-	1.08	original sol-
		8.0	2.48	-	2.60	vent for
		8.0	3.80	-	3.76	extract
		8.0	4.30	±	4.24	
		8.0	5.70	+	5.76	
		8.0	9.60	++	8.32	
		8.0	10.2	++	7.60	
		8.0	16.2	++	0.20	
Water B	6.90	8.0	0.40	-	0.29	Same series
		8.0	1.02	-	1.00	as above but
		8.0	2.48	-	2.52	with 2 inch
		8.0	3.80	-	3.68	dia. filters
		8.0	4.30	-	4.20	
		8.0	5.70	+	5.84	
		8.0	9.60	+	8.66	
		8.0	10.2	+	9.60	
		8.0	16.2	++	0.19	
Water B	7.05	8.0	1.12	-	1.08	Water used as
		8.0	2.06	-	2.00	original sol-
		8.0	2.98	-	3.00	vent for extract
		8.0	3.74	-	3.76	
		8.0	4.68	-	4.72	Sample was
		8.0	5.34	±	5.20	aerated during
		8.0	6.26	+	6.24	testing
		8.0	8.20	+	8.32	
		8.0	10.00	++	8.56	
		8.0	12.8	++	2.44	

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/1	Special Conditions
Atwood - Experiment 4 (continued)						
Water B	7.05	8.0	1.12	-	1.16	Same series as above but with 2 in. dia. filters
		8.0	2.06	-	1.92	
		8.0	2.98	-	2.92	
		8.0	3.74	-	3.68	
		8.0	4.68	-	4.66	
		8.0	5.34	-	4.28	
		8.0	6.26	±	6.38	
		8.0	8.20	+	8.04	
		8.0	10.00	+	9.68	
		8.0	12.8	++	6.20	
Ethanol B	6.40	8.0	0.20	-	0.22	
		8.0	1.00	-	. . .	
		8.0	3.00	-	. . .	
		8.0	5.00	-	. . .	
		8.0	5.25	±	5.20	
		8.0	5.35	±	5.12	
		8.0	5.35	-	5.16	72 hrs. reaction before filtering
		8.0	5.35	-	. . .	0.45μ filter
		6.0	5.35	+	1.28	pH lowered
Ethanol B	6.40	8.0	1.00	-	. . .	Ferric iron used
		8.0	2.00	-	. . .	
		8.0	4.28	+	0.24	
		8.0	4.28	+	0.88	0.45μ filter
Ammonia B	6.60	8.0	1.00	-	. . .	
		8.0	2.00	-	. . .	
		8.0	4.00	±	3.84	
		9.0	4.00	-	. . .	pH raised
		9.0	4.20	+	3.84	pH raised
		8.0	4.20	++	2.52	pH lowered
		8.0	4.20	±	4.12	0.45μ filter
Ammonia B	6.60	8.0	2.04	±	2.00	Ferric iron used

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/1	Special Conditions
Atwood - Experiment 4 (continued)						
HCl B	6.70	8.0	0.40	-	0.42	
		8.0	1.26	+	0.88	
		8.0	1.26	±	1.00	0.45μ filter
		9.0	1.26	±	1.12	pH raised
		6.0	1.26	++	0.20	pH lowered
HCl B	6.70	8.0	0.92	+	0.14	Ferric iron used
Clinton - Experiment 5						
Chloroform A	7.20	8.0	0.30	+	0.24	
Water A - None present						
Ethanol A	7.25	8.0	0.40	-	0.36	
		8.0	1.32	+	0.42	
		9.0	1.32	+	0.64	pH raised
Ammonia A	7.30	8.1	0.20	-	. . .	
		8.0	0.50	-	. . .	
		8.0	1.00	-	. . .	
		8.0	2.16	+	0.70	
		9.0	2.16	+	2.12	pH raised
Ammonia A	7.30	8.0	1.50	-	1.56	Ferric iron
		8.0	2.00	+	0.72	used
HCl A	7.30	8.0	0.20	+	. . .	
Chloroform B	7.20	8.0	0.40	-	0.40	
		8.0	0.68	+	0.16	
Water B	7.20	8.0	0.50	-	. . .	
		8.0	1.00	-	. . .	
		8.0	2.00	-	. . .	
		8.0	3.00	-	. . .	
		8.0	4.00	-	. . .	
		8.0	4.72	±	4.60	
		9.0	4.72	-	4.76	pH raised
		6.0	4.72	+	3.32	pH lowered

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/1	Special Conditions
Clinton - Experiment 5 (continued)						
Water B	7.20	8.1	2.00	-	. . .	Ferric iron
		8.1	3.00	±	2.92	used
Ethanol B	7.05	8.0	0.17	-	0.34	
		8.0	1.08	-	0.92	
		8.0	1.92	-	2.12	
		8.0	3.04	-	3.00	
		8.0	4.00	-	4.04	
		8.0	5.16	±	4.64	
		8.0	5.16	±	5.08	10 min. mix. before filter-ing
		8.0	6.24	+	5.36	
		8.0	7.60	++	2.08	
		8.0	7.60	++	1.04	10 min. mix before filter-ing
Ammonia B	6.95	8.0	1.02	-	0.96	
		8.0	1.88	-	1.88	
		8.0	3.04	-	3.12	
		8.0	4.00	-	3.96	
		8.0	5.28	±	5.28	
		8.0	5.28	±	5.16	10 min. mix before filter-ing
		8.0	6.88	+	5.60	
		8.0	8.78	++	2.96	
		8.0	10.80	++	0.64	
HCl B	7.10	8.0	0.40	-	0.26	
		8.0	1.36	+	0.0	
Chloroform C	6.90	8.0	0.29	±	0.06	
		8.0	1.20	+	0.0	

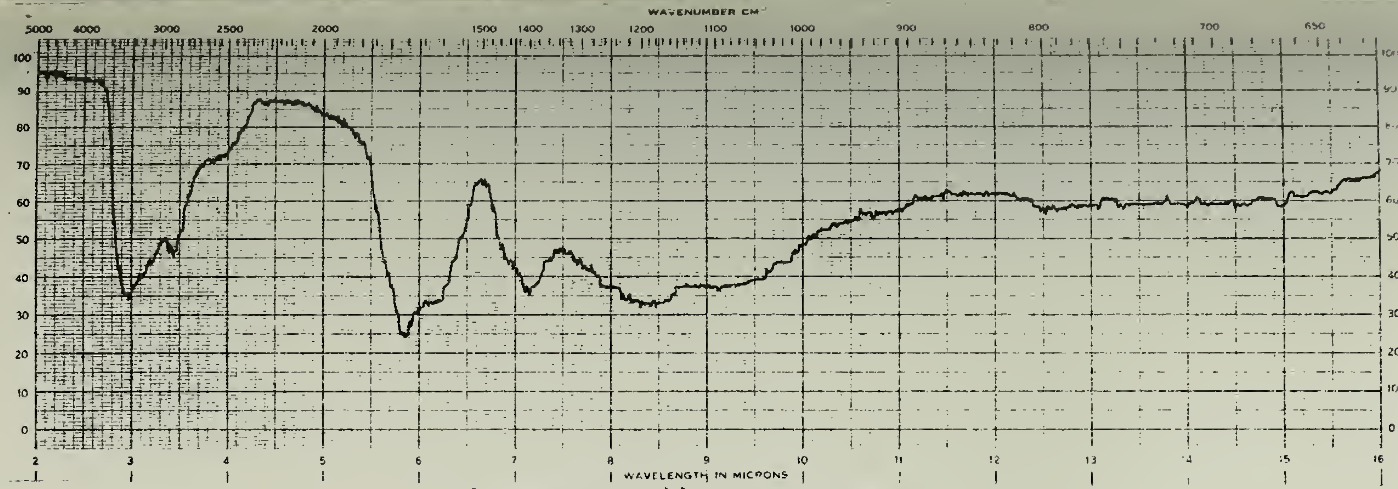
Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Clinton - Experiment 5 (continued)						
Water C	6.70	8.0	0.30	-	0.32	
		8.0	1.12	-	1.04	
		8.0	2.14	-	2.20	
		8.0	3.16	-	3.12	
		8.0	4.42	-	4.08	
		8.0	5.88	±	5.84	
		8.0	5.56	+	4.08	
Ethanol C	6.70	8.0	0.22	-	0.24	
		8.0	2.42	-	2.56	
		8.0	3.84	-	3.80	
		8.0	5.56	±	4.28	
		8.0	7.68	++	2.28	
Ammonia C	7.10	8.0	1.08	-	1.12	
		8.0	3.70	±	3.52	
		8.0	5.06	++	0.24	
HCl C	7.20	8.0	0.24	-	0.20	
		8.0	1.02	-	1.08	
		8.0	2.08	+	0.0	
Control Experiment						
No extract added		8.0	0.30	-	0.30	
		8.0	0.44	±	0.44	
		8.0	0.92	+	0.56	
		8.0	1.28	+	0.20	
		8.0	1.58	+	0.12	
		8.0	2.00	+	0.08	
		8.0	2.30	+	0.08	
No extract added		8.0	0.30	-	0.30	Same series as above with 2 in. dia. filters
		8.0	0.44	-	0.44	
		8.0	0.92	±	0.92	
		8.0	1.28	+	0.68	
		8.0	1.58	+	0.29	
		8.0	2.00	+	0.08	
		8.0	2.30	+	0.08	

Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/1	Iron on Filter	Iron in Filtrate mg/1	Special Conditions
Control Experiment (continued)						
No extract added		8.0	0.48	±	0.46	
		8.0	0.48	+	0.40	10 min. mix before filter-ing
		8.0	0.54	+	0.08	15 min. mix before filter-ing
No extract added		8.0	0.48	-	0.46	Same series as above but with 2 in. dia. filters
		8.0	0.48	-	0.54	
		8.0	0.54	±	0.44	
No extract added		8.0	0.16	±	0.16	Diffused air used
		8.0	0.52	+	0.46	
		8.0	0.52	+	0.36	10 min. mix before filter-ing
		8.0	1.36	++	0.12	
		8.0	1.36	++	0.42	10 min. mix before filter-ing
		8.0	2.10	++	0.22	
		8.0	2.10	++	0.0	10 min. mix before filter-ing
		8.0	2.52	++	0.0	
No extract added		8.0	0.16	-	0.17	Same series as above but with 2 in. dia. filters
		8.0	0.52	±	0.44	
		8.0	0.52	+	0.50	
		8.0	1.36	+	0.60	
		8.0	1.36	+	0.92	
		8.0	2.10	+	0.44	
		8.0	2.10	+	0.33	
		8.0	2.52	+	0.07	

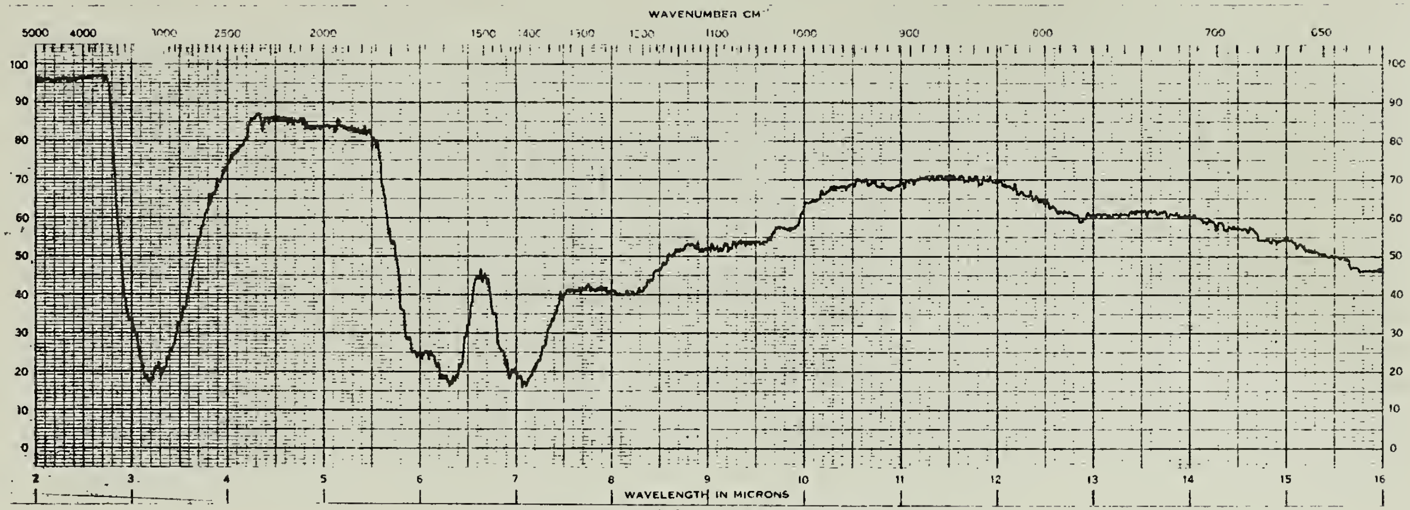
Extract	Initial pH	pH When Filtered	Total Iron in Sol. mg/l	Iron on Filter	Iron in Filtrate mg/l	Special Conditions
Control Experiment (continued)						
Tartaric acid	6.30	8.0	1.02	-	1.12	
		8.0	2.88	-	2.84	
		8.0	5.20	-	5.00	
		8.0	7.28	-	6.92	
		8.0	9.36	-	9.52	
		8.0	11.28	-	11.24	
		8.0	12.44	-	12.24	
Tartaric acid	6.30	8.0	12.44	-	12.04	10 min mix before filtering
		8.0	15.04	±	14.84	
		8.0	15.04	±	15.08	30 min. mix before filtering
		8.0	16.48	+	15.92	
		8.0	19.8	+	19.6	
		8.0	24.4	+	23.5	
		8.0	29.3	++	24.1	
		8.0	33.5	++	5.80	
		8.0	62.6	+++	0.08	
Tartaric acid	6.30	8.0	1.02	-	0.92	Same series as above but with 2 in. dia. filters
		8.0	2.88	-	2.86	
		8.0	5.20	-	5.06	
		8.0	7.28	-	7.28	
		8.0	9.36	-	9.04	
		8.0	11.28	-	11.56	
		8.0	12.44	-	12.08	
		8.0	12.44	-	12.08	10 min. mix before filtering
		8.0	15.04	±	15.00	
		8.0	15.04	±	15.00	30 min. mix before filtering
		8.0	16.48	±	16.48	
		8.0	19.8	+	24.5	
		8.0	24.4	+	24.2	
		8.0	29.3	+	20.7	
		8.0	33.5	++	22.9	
		8.0	62.6	++	0.07	

APPENDIX C

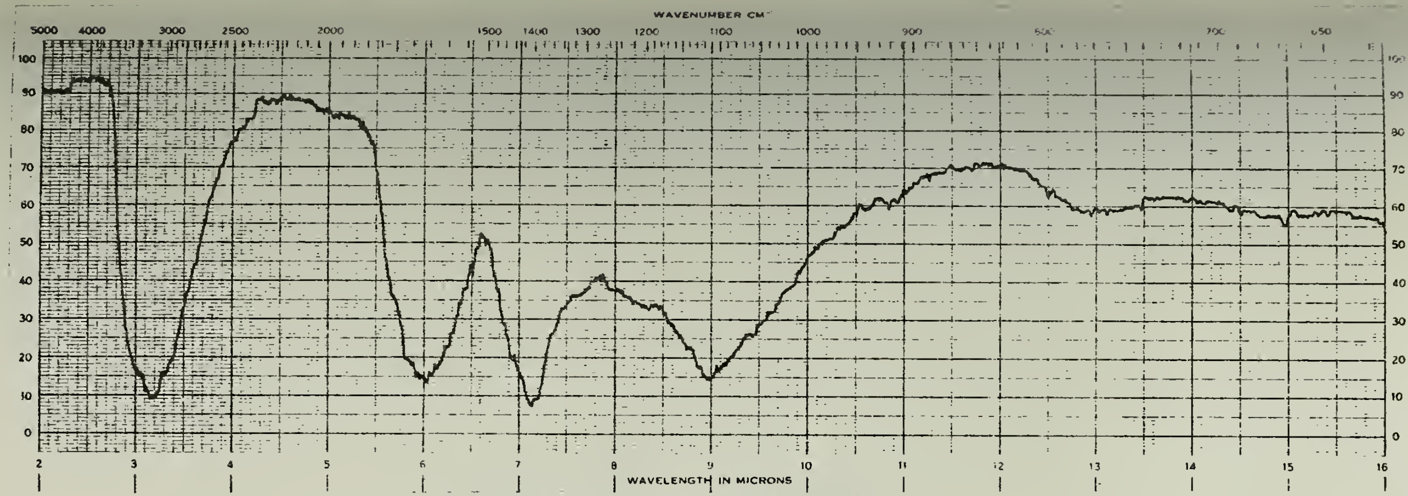
INFRA-RED SPECTROGRAPHS



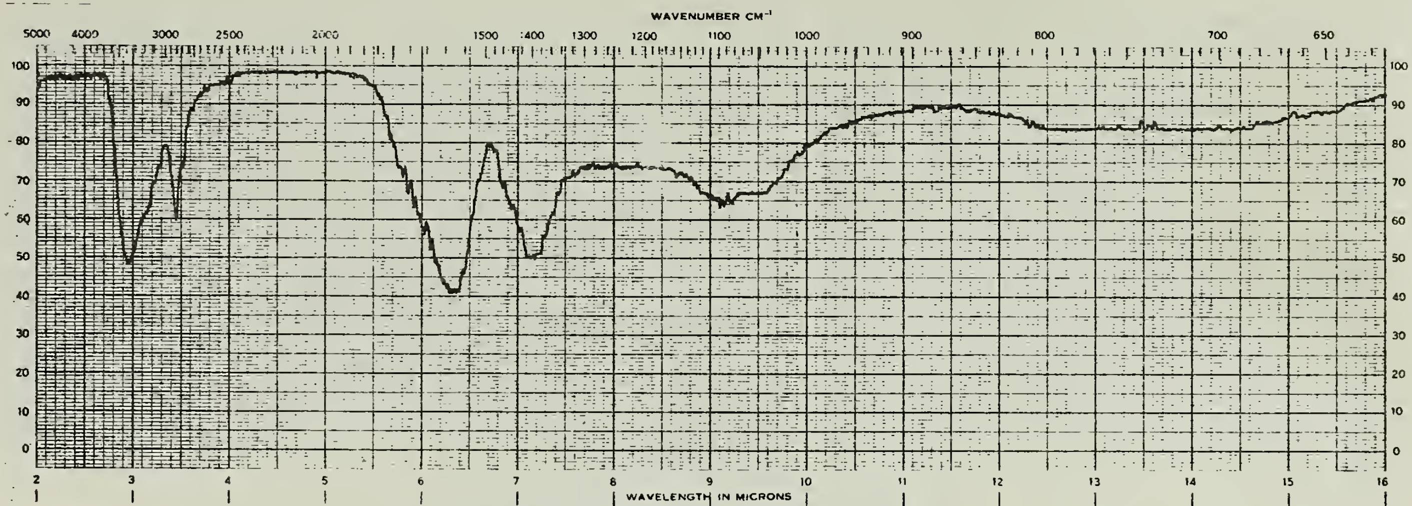
OAKWOOD (I) - ETHANOL B



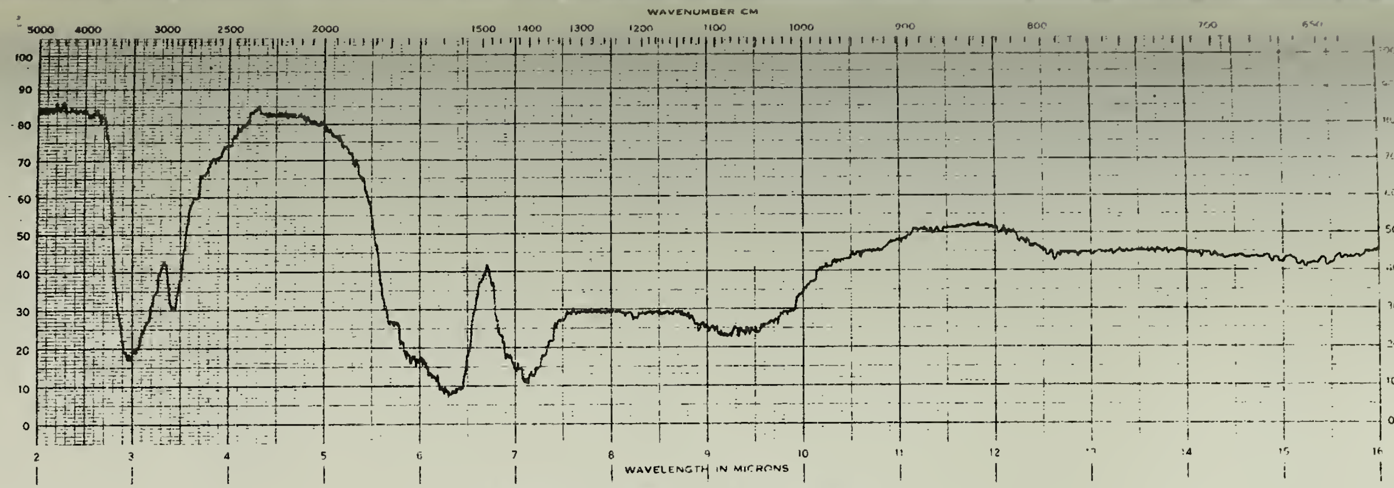
OAKWOOD (I) - AMMONIA B



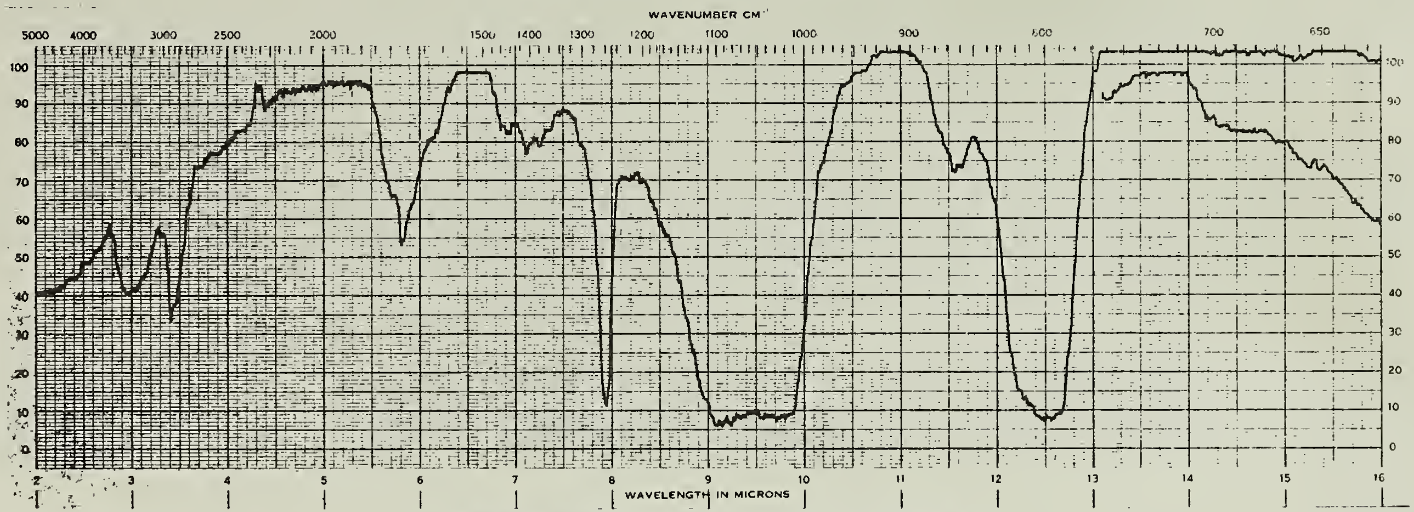
PHILO (2) - AMMONIA A



ATWOOD (4) - WATER A



CLINTON (5) - ETHANOL A



CLINTON (5) - CHLOROFORM A

APPENDIX D

LOG OF OXIDATION STUDY

Extract	Lapsed Time After Aeration Min.	Ferrous Iron Before Filtration mg/1	Total Iron After Filtration mg/1	pH of Test Sol.	Dissolved Oxygen in Test Sol. mg/1
Philo - Raw water:	Total Iron: 0.66 mg/1 Alkalinity: 227 mg/1 as $CaCO_3$.				
No extract added	Before air.	0.66	0.66	7.48	0.25
	0	0.54	0.32	7.75	
	3	0.30	0.26	7.78	7.20
	10	0.20	0.18	7.77	
	20	0.06	0.10	7.77	
	35	0.04	0.06	7.78	
	50	0.0	0.04	7.78	
Ammonia B 5 mg/1	Before air.	0.50	0.52	7.54	0.30
	0	0.45	0.48	7.90	
	3	0.32	0.24	7.92	7.30
	10	0.04	0.12	7.94	
	20	0.04	0.20	7.94	
	32	0.04	0.06	7.94	
Tartaric Acid 5 mg/1	Before air.	0.40	0.60	7.70	0.30
	0	0.26	0.56	7.98	
	3	0.26	0.60	8.00	7.40
	10	0.12	0.58	8.00	
	20	0.10	0.60	8.00	
	35	0.08	0.46	8.00	
	55	0.06	0.30	8.00	
	75	0.04	0.18	7.96	
	105	0.04	0.18	7.93	
Clinton - Raw water:	Total Iron: 1.88 mg/1 Alkalinity: 4.30 mg/1 as $CaCO_3$				
No extract added	Before air.	1.85	2.04	7.56	0.05
	0	1.18	0.96	7.83	
	3	0.71	0.80	7.88	6.70
	10	0.22	0.10	7.89	
	18	0.18	0.14	7.89	
	26	0.0	0.0	7.89	

xtract	Lapsed Time After Aeration Min.	Ferrous Iron before Filtration mg/l	Total Iron After Filtration mg/l	pH of Test Sol.	Dissolved Oxygen in Test Sol. mg/l
linton (continued)					
artaric Acid	Before air.	1.95	1.88	7.61	
mg/l	0	1.25	1.68	7.82	
	3	0.78	1.84	7.83	6.70
	10	0.22	1.32	7.82	
	18	0.17	1.00	7.82	
	28	0.06	0.60	7.82	
	38	0.10	0.68	7.82	
nmonia B	Before air.	2.02	1.88	7.58	
kp. 5	0	1.25	1.00	7.85	
mg/l	3	0.75	0.36	7.85	6.75
	10	0.21	0.30	7.85	
	18	0.17	0.0	7.85	
	26	0.03	0.16	7.85	
nmonia B	Before air.	2.04	1.72	7.65	0.05
kp. 5	0	1.15	1.68	7.80	
mg/l	3	0.63	1.16	7.80	6.60
	10	0.19		7.80	
	18	0.10	0.16	7.80	
	26	0.03	0.0	7.80	

VITA

Lloyd R. Robinson, Jr. was born April 13, 1931 in Kansas City, Missouri, and received his primary and secondary education in that community.

He attended Kansas City, Missouri, Junior College and received the A. S. Certificate in 1950. He then attended the University of Kansas where he received the B. S. Degree in Civil Engineering in 1953. During the summer of 1952, he was employed as an Engineering Assistant at Black and Veatch, Consulting Engineers.

He was commissioned as an Ensign in the Civil Engineer Corps, U. S. Naval Reserve, in July, 1953 and served first as a personnel officer and then as a transportation officer before his release from active duty in 1956.

In 1956 he accepted a position as Instructor in Civil Engineering and part-time graduate student at the University of Kansas. During the summer of 1957, he served as a Junior Engineer for the Kansas State Board of Health. In 1958 he received the M.S. Degree in Civil Engineering.

He then accepted a position in the Plans and Grants Section of the Water Pollution Control Division of the Texas State Health Department. He resigned this position in January, 1960 to accept a position as Research Assistant at the University of Illinois. During this period, he was also a part-time graduate student. During the school year 1961-62,

he pursued his studies full-time with the aid of a Traineeship from the U. S. Public Health Service.

He is presently an Assistant Professor of Civil Engineering at New Mexico State University.

He is a Member of the Society of the Sigma Xi, the American Water Works Association, the Water Pollution Control Federation, the American Society for Engineering Education, an Associate Member of the American Society of Civil Engineers, and a Lieutenant in the Civil Engineer Corps, U. S. Naval Reserve.

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